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Inversion Amalgam Chronopotentiometry

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The review deals with the theoretical principles of the method of inversion amalgam chronopotentiometry. The transition times and the potential-time relations for the electrochemical dissolution of amalgams under galvanostatic conditions are analysed and the applications of the method in electroanalytical practise, in the study of the kinetics of electrode processes and adsorption, in the determination of the numbers of electrons involved in the reaction and diffusion coefficients, and in the study of complex formation, corrosion of amalgams, etc. are examined in detail. The fundamentals of the theory of electrode processes complicated by preceding, subsequent, and simultaneous chemical reactions are described. The possibilities and advantages of the method of amalgam chronopotentiometry in relation to other electrochemical procedures are indicated.
The bibliography includes 86 references.

CONTENTS

I. INTRODUCTION

One of the promising methods for the determination of low concentrations of elements and for the investigation of the kinetics of electrode processes on amalgams is that of inversion amalgam chronopotentiometry (MIAC). The studies carried out hitherto have shown that this method is distinguished by the simplicity of the apparatus employed and of the mathematical treatment of the physicochemical relations. The latter factor makes it irreplaceable in the investigation of the chemical reactions accompanying the electrode process. The linear chronopotentiometric plot has already been used widely for these purposes, but the number of studies on the applications of inversion amalgam chronopotentiometry in the investigation of the kinetics of electrode processes and for the determination of microconcentrations of elements is still small. This is probably due to the novelty of the method (the first studies by this method were published in 1966) and the lack of a review dealing with the method.

II. THE METHOD OF INVERSION AMALGAM CHRONOPOTENTIOMETRY

The method of inversion amalgam chronopotentiometry (or simply amalgam potentiometry) is a variety of the galvanostatic method, the fundamental principles of which have been described[1,2]. In this method analysis of the transition times and of the shape of the potential-time curve yields information about the presence of the depolariser in the amalgam and the physicochemical characteristics of the electrode process are determined.

The galvanostatic method was used for the first time to investigate the electrochemical dissolution of amalgams by Zbinden[3]. He demonstrated the possibility of determining copper at concentrations down to 10^{-8} M in the electrochemical dissolution of copper amalgam. The stepwise variation of the current and chemical dissolution on open circuit were used by Bruckenstein and Nagai[4] to determine thallium and lead at concentrations of 2×10^{-7} M. They obtained the amalgam at a rotating platinum electrode.

The method of inversion amalgam chronopotentiometry, which is essentially a new electrochemical procedure, has been put forward in a number of investigations[5-9]. Three stages must be distinguished in this method.

1. Preliminary electrolysis. The metal in the solution is concentrated in the mercury electrode at a specified potential with formation of an amalgam or a sparingly soluble deposit.
2. Period without stirring. After pre-electrolysis, the solution is allowed to stand for 30–60 s; the flux from the electrode then becomes virtually zero[10].
3. Electrochemical dissolution of the metal from the amalgam when a direct current is passed through the electrode. Under these conditions, the pen recorder draws the curve (chronopotentiogram) characterising the time variation of the electrode potential (Fig. 1).

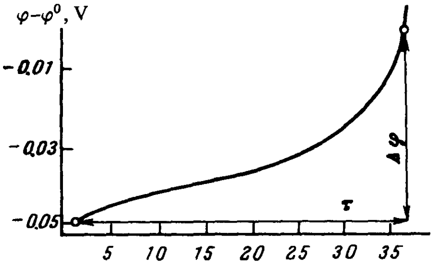

Figure 1. Theoretical chronopotentiometric curve.

If the electrochemical dissolution takes place in a stirred electrolyte, the system is allowed to stand until the attainment of the equilibrium (more precisely the initial) potential of the amalgam. The electrochemical-concentration and the solution-at-rest stages have been examined[10,11]. According to these investigations[10,11], a uniform distribution of the metal throughout the bulk of the electrode is observed towards the end of the second stage. This conclusion played an appreciable role in the formulation of the initial condition in the theory of inversion amalgam voltamperometry.

The usual circuit for galvanostatic measurements is assembled for recording chronopotentiometric curves in MIAC[1,2]. Two types of electrodes are used in the method: a mercury film electrode (stationary or rotating) and a stationary spherical mercury electrode consisting of a mercury drop with a radius not exceeding 0.1 cm. The mercury film electrode consists of a film of mercury between 4 and 20 μm thick deposited on a polished surface of the end-face of a silver wire 1–2 mm in diameter. The silver wire is pressed into a Teflon cylinder ($d \simeq$ 8 mm). A hermetically sealed three-electrode cell is used for the experiments. When a rotating disc electrode is employed, provision is made for a system regulating the rate of rotation (stepwise or continuous)[12]. The rates of rotation of the electrode employed usually do not exceed 10 000 rev min^{-1}.

III. THEORY OF THE METHOD IN THE ABSENCE OF KINETIC COMPLICATIONS

1. Expressions for the Transition Time

Suppose that a simple first-order electrochemical reaction

$$\mathrm{M(Hg)} \rightleftarrows \mathrm{M}^{z+} + ze$$

takes place at the electrode. We assume that there is an excess of an indifferent electrolyte in the solution, that the ψ_1 potential is negligibly small and independent of the cell potential, that there is no specific adsorption of the starting materials and products, and that the oxidised form of the electrochemically active substance is soluble in the electrolyte solution. We shall bear in mind that the reduced form of the electrochemically active substance diffuses under the conditions of restricted diffusion, i.e. during the measurement of the curve the diffusion layer extends throughout the entire volume of the electrode. The diffusion of the ions formed during the electrochemical dissolution of the amalgam from the surface of the electrode will occur under the conditions of a semi-infinite volume[13]. This is valid for $L_X \geqslant \sqrt{D_0 \tau}$, where L_X is the distance from the electrode surface to the wall of the electrolytic cell, D_0 the diffusion coefficient of the ions in solution, and τ the transition time. This condition is almost always fulfilled with the exception of thin-layer electrolysers.

In the electrochemical dissolution of the amalgam at a constant current density i the equations for the distribution of the concentration of the metal atoms are of the following form:

$$c^s_{\mathrm{R,f}} = c^0_R - j_R\left[v_R + \frac{1}{3} - 2\sum_{n=1}^{\infty}\frac{\exp(-\mu_n^2 v_R)}{\mu_n^2}\right], \tag{1}$$

on the surface of the mercury film electrode[5,14], where $\mu_n = n\pi$, $n = 1, 2, 3, \ldots$, $v_\mathrm{R} = D_\mathrm{R}t/l^2$, and t the time;

$$c^s_{\mathrm{R,s}} = c^0_R - j_R\left[3v_R + \frac{1}{5} - 2\sum_{n=1}^{\infty}\frac{\exp(-\bar{\mu}_n^2 v_R)}{\bar{\mu}_n^2}\right], \tag{2}$$

on the surface of a spherical mercury electrode[9], where $\bar{\mu}_n$ are the roots of the transcendental equation $\tan\bar{\mu}_n = \bar{\mu}_n$. In Eqns. (1) and (2) $j_\mathrm{R} = q_\mathrm{R}y_0/D_\mathrm{R}$, $q_\mathrm{R} = i/zF$, q_R is the flux from the electrode, z the number of electrons participating in the electrode process, F the Faraday, c^0_B the initial concentration of the metal in the amalgam, y_0 the characteristic dimension of the electrode ($y_0 = l$ for the mercury film electrode and $y_0 = r_0$ for the spherical electrode), and D_R the diffusion coefficient of metal atoms in mercury.

Eqns. (1) and (2) have been analysed in detail in a number of reports[14-16]. For large values of t, the exponential terms in these equations may be neglected. The following equations are valid (to within at most 1%)

for the mercury film electrode with $v_R \geqslant 0.35$ (when $D_R = 10^{-5}$ cm^2 s^{-1} and $l \leqslant 10^{-3}$ cm, we then have $t \geqslant 0.035$ s) and for the spherical electrode with $v_R \geqslant 0.14$ (when $r_0 \leqslant 5 \times 10^{-2}$ cm and $D_R = 10^{-5}$ cm^2 s^{-1}, we then have $t \geqslant 35$ s):

$$c^s_{\mathrm{R,f}} = c^0_R - j_R\left(v_R + \frac{1}{3}\right) \tag{3}$$

and

$$c^s_{\mathrm{R,s}} = c^0_R - j_R\left(3v_R + \frac{1}{5}\right). \tag{4}$$

When $v_R \geqslant 34$ (when $D_R = 10^{-5}$ cm^2 s^{-1} and $l \leqslant 10^{-3}$ cm, we have $t \geqslant 3.4$ s), Eqn. (3) reduces to

$$c^s_{\mathrm{R,f}} = c^0_R - j_R v_R. \tag{5}$$

Since the time required to record chronopotentiograms is usually greater than 5 s, Eqn. (5) may be used.

The expression for the transition time τ is determined by the condition $c_R(1, v'_R) = 0$, where $v'_R = D_R\tau/y_0^2$. From Eqns. (3), (4), and (5), we obtain for the film electrode

$$\tau = \frac{zFlc^0_R}{i} - \frac{l^2}{3D_R}, \tag{6}$$

$$\tau = \frac{zFlc^0_R}{i}, \tag{7}$$

and for the spherical electrode

$$\tau = \frac{zFlc^0_R}{3i} - \frac{r_0^2}{15D_R}. \tag{8}$$

Analysis[14-16] of Eqns. (6)–(8) leads to the following conclusions: (1) the transition time for electrodes of both types is directly proportional to the concentration of the metal in the amalgam c^0_R (this relation is used in electroanalytical practise); (2) according to Eqn. (7), the product $i\tau$ is independent of current density and is proportional to the amount of metal in the amalgam; (3) the independence of $i\tau$ of current density constitutes a criterion of the absence of a preceding chemical stage; (4) Eqn. (8) may be used to find the diffusion coefficient of the metal atoms in the amalgam; (5) the form of the relation between τ and i makes it possible to investigate the adsorption of surface-active substances on the electrode.

Table 1. The transition times in inversion amalgam chronopotentiometry with film (τ_1) and spherical (τ_2) electrodes and in chronopotentiometry under the conditions of linear semi-infinite diffusion (τ_3) ($z = 2$, $l = 10^{-3}$ cm, $r_0 = 0.06$ cm, $D_R = 10^{-5}$ cm^2 s^{-1}; the degree of concentration of the metal in the mercury film electrode was assumed to be 1000*).

$10^{-7}c^0_O$, g-ion cm^{-3}	$10^{-5}i$, A cm^{-2}	τ_1, s	τ_2, s	τ_3, s	$\frac{\tau_1}{\tau_2}$	$\frac{\tau_1}{\tau_3}$
1	4	480	6	1.6	80	300
2	2	960	12	6.4	80	150
4	1	1920	24	25.6	80	75

* The degree of concentration of the metal in the mercury film electrode usually exceeds this value[14].

The expressions for the transition time in amalgam chronopotentiometry differ from those in the usual chronopotentiometry[1] (under the conditions of semi-infinite diffusion). Table 1 lists the calculated values of τ for chronopotentiometry under the conditions of restricted linear and spherical diffusion (amalgam chronopotentiometry) and semi-infinite linear diffusion. Evidently, other conditions being equal, the transition time in amalgam chronopotentiometry is much longer than in direct chronopotentiometry (under the conditions of semi-infinite diffusion), the difference decreasing with increasing concentration or with decreasing current density. Table 1 demonstrates the clear advantages of the mercury film electrode (in relation to analytical practise).

2. Equations of Chronopotentiometric Curves

For a reversible electrode process, the equation of the chronopotentiometric curve is (in terms of the diffusion overvoltage–time variables)[14-17]

$$\eta_d = \frac{2{,}3\,RT}{zF} L_O, \tag{9}$$

where

$$L^f_O = \lg[v'_R/(v'_R - v_R)]\,(1 + 2j_0v_0^{1/2}/\pi^{1/2}c^0_O)$$

for the mercury film electrode ($v'_R \geqslant 3.4$), T is the absolute temperature, c^0_O the initial concentration of the metal ions in solution and

$$j_0 = \frac{il}{zFD_0};\; v_0 = \frac{D_0t}{l^2}.$$

For the spherical mercury electrode ($v'_R \geqslant 0.14$), we have

$$L^s_O = \lg\frac{(3v'_R + 0{,}2)}{3(v'_R - v_R)}\left[1 + \frac{j_0}{c^0_O}(1 - \exp v_0 \cdot \operatorname{erfc} v_0^{1/2})\right].$$

The plot of η_d against L_O is a straight line with a slope of $2.3RT/zF$. This serves as a criterion of the reversibility of the electrode process[17]; agreement between the theoretical and experimental values shows that the electrode process is reversible.

At high overvoltages ($\eta \gg RT/zF$) the irreversible electrochemical reaction $M(Hg) \rightarrow M^{Z+} + ze^-$ takes place and the equation of the chronopotentiometric curve simplifies greatly[14-17]:

$$\eta_{ir} = \frac{2{,}3\,RT}{\beta zF}\left(\lg\frac{i}{i_0} - L_{ir}\right), \tag{10}$$

where

$$L^f_{ir} = \lg\frac{v'_R - v_R}{v'_R} \text{ and } L^s_{ir} = \lg\frac{3(v'_R - v_R)}{(3v'_R + 0{,}2)}.$$

Hence the slope of the plot of η_{ir} against L_{ir} is βz; the exchange current density i_0 and hence the rate constant for the electrode process k_S may be found from the initial overvoltages taking into account the relation

$$k_S = \frac{i_0}{zF\,(c^0_O)^\beta\,(c^0_R)^\alpha}, \tag{11}$$

where α and β are the transfer coefficients for the cathodic and anodic processes respectively.

The main factors which determine the applicability of Eqns. (9) and (10) are the exchange current density, the overvoltage, and the transition time[14]. With decrease of i and η and with increase of τ, the processes shift towards reversibility and conversely.

A numerical estimate yields

$$4 \cdot 10^{-2} \geqslant k_S \geqslant 4 \cdot 10^{-5}. \tag{12}$$

The intermediate values of k_S correspond to a quasireversible (quasidiffusional) electrode process. A more detailed analysis of chronopotentiometric curves has been given elsewhere[14-17].

Some problems of amalgam chronopotentiometry at a mercury film electrode have also been examined by Igolinskii and Igolinskaya[18] and at a spherical mercury electrode by Galus[19] and Baranski[20].

All the above equations were obtained without taking into account the influence of the structure of the electrical double layer. In order to allow for the electrical double layer[21], the quantity ψ_1 must be introduced into the fundamental equation of electrochemical kinetics. If it is assumed that the electrode potential is distributed over the series-connected capacitances of the dense (C) and diffuse (C_d) components of the double layer and that the capacitance is independent of potential in the range of values of the latter corresponding to the chronopotentiometric curve, then

$$\psi_1 = \frac{C}{C_d}(\varphi - \varphi_0), \tag{13}$$

where φ_0 is the zero-charge potential.

The method of cyclic chronopotentiometry[1] (with current reversal), which makes it possible to investigate both the anodic and cathodic processes, is convenient for the study of the kinetics of electrode processes. The theory of amalgam chronopotentiometry with current reversal has been discussed[22,23]. The equations were derived on the assumption that the direction of the current is reversed at the instant of attainment of the transition time and that the current density is not equal to that in the cell before reversal. If a reduction process takes place after an oxidation process, then analysis of the theoretical relations gives rise to the following expression, which is simplest when the current densities for the forward and reverse processes are equal:

$$\tau = \frac{4}{3}\tau_1, \tag{14}$$

where τ_1 is the transition time of the oxidation process.

The characteristic points[23] on the cathodic branch of the chronopotentiometric curve in amalgam chronopotentiometry for a mercury film electrode are $\tau/4$ and 1.0716τ.

An interesting variety of the method of amalgam chronopotentiometry has been proposed[24-26], namely amalgam chronopotentiometry with a programmed current. Cases have been examined where the current was specified in the form of linear, exponential, and sinusoidal functions. The sinusoidal form of the specified current may find the greatest number of practical applications (under these conditions, the error in the determination of the transition time is fully excluded).

3. The Influence of the Charging of the Electrical Double Layer in Amalgam Chronopotentiometry

In the chronopotentiometric method a proportion of the charge supplied to the electrode is required to charge the electrical double layer (e.d.l.), which results in a discrepancy between the experimental and theoretical (obtained without allowance for the charging of the electrical double layer) relations[1]. Using the method of integral equations, de Vries[27] analysed theoretically the influence of the charging of the e.d.l. on chronopotentiometric curves for the electrochemical dissolution of amalgams from a mercury film electrode on the hypothesis that a diffusion-controlled process takes place at the electrode and that the e.d.l. capacitance is independent of the potential.

Using the Huber method, he solved the integral equation. The theoretical φ–t curves, calculated for certain values of K_C and h (see below), are presented in Fig. 2, while Table 2 lists the calculated shifts of the chronopotentiometric curves ($\Delta\varphi_{\tau/4}$) with and without allowance for the charging of e.d.l. Here $K_C = (RT/zF)C_d[c_R^0(\pi D_R\tau_\infty)^{1/2}]^{-1}$ is a parameter characterising the distortion of the chronopotentiometric curve, $h = l^2/D_R\tau$, $\lambda = t/\tau_\infty$, and τ_∞ is the transition time under the conditions of semi-infinite diffusion without allowance for the charging of e.d.l.

Table 2 shows that the error in the determination of the transition time is less than 4% for $h > 0.3$. This value of h characterises the applicability of the Delahay-Mattax method[1], which has been used here to determine the transition time. With decrease of h, the error in the determination of the transition time increases and the distorting influence of the e.d.l. capacitance becomes more appreciable (Fig. 2); the Delahay-Mattax method becomes unsuitable under these conditions. Fig. 2 shows that, with increase of the e.d.l. capacitance, the chronopotentiometric curves shift along the potential axis with a simultaneous change in the slope of the initial and final sections of the curve, the two being equal.

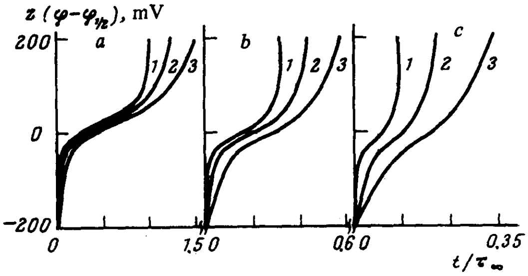

Figure 2. Theoretical φ–t curves for a mercury film electrode calculated taking into account the charging of the electrical double layer for different values of K_C [1) 0; 2) 0.003; 3) 0.0075] and three values of h [a) $h = \infty$; b) $h = 0.1$; c) $h = 0.01$].

De Vries[27] analysed in detail the case where $h \to 0$ (the case of thin films and large values of τ). The Delahay-Mattax graphical method may be applied in the potential range −200 – +200 mV subject to the condition that a horizontal line, parallel to the time axis, divides the distance between the initial and final sections of the curve in proportions of 0.382 : 0.618. The error in the measurement of the transition time under these conditions is not more than ±4% for $K_C \leqslant 0.01$ and $h \leqslant 0.1$.

The order of magnitude of the error due to the charging of the e.d.l. can be estimated approximately by Hirst's method[1]:

$$\frac{Q_C}{Q_\varphi}=\frac{C_d\Delta\varphi}{i\tau}, \tag{15}$$

where $\Delta\varphi(V)$ is the width of the chronopotentiogram. Evidently the error is smaller the higher the current density and the concentration of the electrochemically active substance. For example, when $C_d = 20\ \mu F\ cm^{-2}$, $\Delta\varphi = 0.1 V$, $D_R = 10^{-5}\ cm^2\ s^{-1}$, $z = 2$, and $c_R^0 = 10^{-6}$ g-atom cm^{-3}, the current density should not exceed 0.1 A cm^{-2} for a permissible error of 1%.

Table 2. The results of the calculation of the influence of the charging of the electrical double layer on the characteristics of the chronopotentiometric curves ($\Delta\varphi_{T/4}$ is the shift of the chronopotentiometric curve).

	$z\,(\Delta\varphi_{\tau/4})$, mV			Error in the determination of λ, %	
hK_c	0	0.003	0.0075	0.003	0.0075
	0	−1.7	−2.6	−1.7	1.9
$h=3$	−0.6	−2.4	−3.0	0	2.4
$h=1$	−5.6	−7.3	−7.9	0.5	3.5
$h=0.3$	−14.4	−15.8	−16.3	1.5	5.6

IV. APPLICATIONS OF THE METHOD OF AMALGAM CHRONOPOTENTIOMETRY

1. Oxidation of a Multicomponent Amalgam

If the chronopotentiometric half-wave potentials differ appreciably, several steps are observed on the potential–time curve. The system of equations describing the distribution of the concentrations of the elements at the surface of the mercury film electrode is[14-16,28-30]

$$\sum_{k=1}^{m} c_{R,k}^{S}=\sum_{k=1}^{m}\left\{c_{R,k}^{0}-j_{R,k}\left[v_{R,k}+\frac{1}{3}-2S_1(v_{R,k})\right]\right\}. \tag{16}$$

We shall consider the electrochemical oxidation of a two-component amalgam, where the following reactions take place at the electrode:

$$M_1(\mathrm{Hg})\rightarrow M_1^{z_1+}+z_1e,$$
$$M_2(\mathrm{Hg})\rightarrow M_2^{z_2+}+z_2e.$$

The metal M_2 is oxidised at more positive potentials. When the transition time τ_1 is reached, M_2 begins to react, while M_1 continues to diffuse to the electrode surface, where it is oxidised simultaneously with M_2. If M_1 is fully oxidised during the time τ_1, then it has no influence on the transition time of M_2.

The fraction of the residual metal M_1 in the amalgam after the time τ_1 may be found from the formula[14,29]

$$p=\frac{il}{z_1Fc_R^0D_R}. \tag{17}$$

It follows from Eqn. (17) that the fraction of the residual metal in the mercury film increases with increasing film thickness and polarising current density. We shall estimate p for the following conditions: $i = 2\times10^{-4}$ A cm^{-2}, $l = 2\times10^{-3}$ cm, $S = 6\times10^{-2}\ cm^2$, $D_R = 10^{-5}\ cm^2\ s^{-1}$, and $c_R^0 = 2\times10^{-6}$ g-atom cm^{-3}, whereupon $p = 0.04$. Under the above conditions, $\tau = 5$ s. Usually $\tau > 5$ s and $l < 2\times10^{-3}$ cm and p is then less than 0.01.

Consequently when the curves are drawn by a pen recorder during the transition time, almost the entire metal dissolves from the mercury film. The constancy of $i\tau$ over a wide range of variation of the polarising current (from 7.5×10^{-7} to 1.4×10^{-5} A) has been demonstrated experimentally[14] in relation to the oxidation of cadmium (1 M KCl), lead (1 M KNO_3), and indium (0.5 M $HClO_4$) amalgams. This implies that, under the conditions of amalgam chronopotentiometry, the metal emerges almost completely from the mercury film.

Using the method of additive functions, Pnev and Zakharov[30] arrived at the following expression when they considered the oxidation of a two-component amalgam:

$$\tau_2-\frac{2l^2}{D_R}\left[S_1(\tau_1+\tau_2)-S_1(\tau_1)\right]=\frac{z_2Flc_{R,2}^0}{i}, \tag{18}$$

where

$$S_1(\tau_1+\tau_2)=\sum_{n=1}^{\infty}\frac{\exp\left[-\mu_n^2\left(v_{R_1}+v_{R_2}\right)\right]}{\mu_n^2};$$
$$S_1(\tau_1)=\sum_{n=1}^{\infty}\frac{\exp\left(-\mu_n^2v_{R_1}\right)}{\mu_n^2}.$$

It follows from the last equation that, for a fairly large value τ_1 (for $v_R' \geqslant 0.35$), when the sums $S_1(\tau_1+\tau_2)$ and $S_1(\tau_1)$ may be neglected, the transition time for the oxidation of the succeeding element (M_2) is independent of the transition time for the oxidation of the previous element (M_1). For spherical diffusion, this conclusion is valid when $v_R' \geqslant 0.14$ (see above). The theoretical results obtained have been confirmed for the oxidation of thallium and lead amalgams in the presence of zinc and for a thallium amalgam in the presence of cadmium[14,28].

Table 3. Data for the determination of the number of electrons involved in the reaction by amalgam chronopotentiometry.

Element	$10^3 i\tau_{exp}$, C	$10^3 i\tau_{theor}$, C	z_{exp}	z_{theor}
Pb	2.65	2.80	1.9	2
Cd	2.87	2.92	2.0	2
In	2.02	2.2	2.8	3

Under the conditions of semi-infinite diffusion, the mutual influence of the elements is observed when they are present jointly in solution, which hinders their accurate quantitative determination[1].

2. Determination of the Number of Electrons Involved in the Electrode Reaction

Using Eqn. (7), it is possible to determine the number of electrons z and to reach appropriate conclusions concerning the mechanism of the electrode reaction. This method has been used in the determination of the number of electrons involved in the electrochemical oxidation of lead (1 M KNO_3), cadmium (1 M KCl), and indium (0.5 M $HClO_4$) amalgams[14]. The observed values of z agree with the theoretical values (Table 3). The determination of the number of electrons from the chronopotentiometric curve is discussed below.

3. Determination of the Diffusion Coefficients of Metal Atoms in Mercury

As stated above, the diffusion coefficients of metal atoms in mercury can be found by analysing Eqn. (8)†.

According to Eqn. (8), the plot of τ against $1/i$ is a straight line, which makes an intercept $r_0^2/15D_R$ on the τ axis. Knowing r_0, it is possible to calculate the diffusion coefficient of metal atoms in mercury.

4. Investigation of the Kinetics of the Ionisation of Amalgams. The Use of the Rotating Disc Electrode

Eqns. (9) and (10) have been used[17] to investigate the electrochemical dissolution of thallium, lead, bismuth, and indium amalgams at a mercury film electrode. It was established that the electrochemical oxidation of thallium, bismuth, and lead amalgams in the corresponding supporting electrolytes (Table 4) is reversible, while that of indium and bismuth amalgams in perchloric acid solutions is irreversible (Table 5).

Table 4. The results of the study of the electrochemical dissolution of thallium, lead, and bismuth amalgams at a stationary mercury film electrode and a rotating mercury disc electrode (n_{rev} = 1200 rev min^{-1}) at 293 K.

Amalgam	Supporting electrolyte	φ^0, V	2.3 RT/zF, V		
			experimental values		Theoretical values
			stationary electrode	disc electrode	
Tl	1 M KNO_3	−0.484	0.060	0.059	0.058
Pb	1 M KNO_3	−0.374	0.030	0.029	0.029
Bi	1 M HNO_3	−0.008	0.020	0.0215	0.0194

Table 5. The results of the study of the kinetics of the electrochemical oxidation of bismuth and indium amalgams at a stationary mercury film electrode.

Amalgam	Supporting electrolyte	$10^5 c_O^0$, M	$10^5 i$, A	τ, s	$\frac{2.3RT}{\beta zF}$, V	βz	$10^4 i_0$, A cm^{-2}	k_S, cm s^{-1}
In	2 M $HClO_4$	1,0	0.9	20.0	0.0277	2.1	0.9	$4\cdot10^{-5}$
Bi	1 M $HClO_4$	1.0	1.3	25.0	0.0233	2.49	1.83	$2\cdot10^{-4}$

Kinetic studies can be carried out very conveniently at a rotating electrode[12], whereby it is possible to take into account exactly concentration polarisation. The rotating disc electrode has been used in inversion amalgam chronopotentiometry to investigate the kinetics of the electrochemical dissolution of amalgams[31]. It has been stated[32,33] that amalgam chronopotentiometry with a rotating disc electrode is distinguished by the simplicity of the interpretation of the results. If the treatment is based on the general kinetic discharge–ionisation equation[21], then the equation of the chronopotentiometric curve for the electrochemical dissolution of the metal from the amalgam on the rotating disc electrode is

$$\eta = \frac{2{,}3\,RT}{\beta zF}\left(\lg\frac{i}{i_0} - L_{\text{k}}\right), \tag{19}$$

where

$$L_{\text{k}} = \lg\left[\frac{v'_R - v_R}{v'_R} - \left(1 + \frac{j_0}{c_O^0}\right)e^{-\frac{zF}{RT}\eta}\right] \tag{20}$$

is the thickness of the boundary diffusion layer on the rotating disc, $j_0 = i\delta/zFD_O$, $\delta = 0.642\,D_O^{1/3}\nu^{1/6}n_{\text{rev}}^{-1/2}$), and n_{rev} the rate of rotation of the electrode (rev s^{-1}).

At fairly high overvoltages (but not such that an irreversible electrode process can occur), the η – L_{k} curve becomes a straight line with a slope of 2.3 $RT/\beta zF$ (Fig. 3). Evidently, with increase of the rate of rotation of the electrode (with decrease of the parameter j_0/c_O^0), the curve is transformed into a straight line at lower overvoltages. The limiting case corresponds to $j_0/c_O^0 \ll 1$. This factor makes it possible to simplify the analysis of chronopotentiometric curves. Hence the advantage of amalgam chronopotentiometry using a rotating disc electrode is evident.

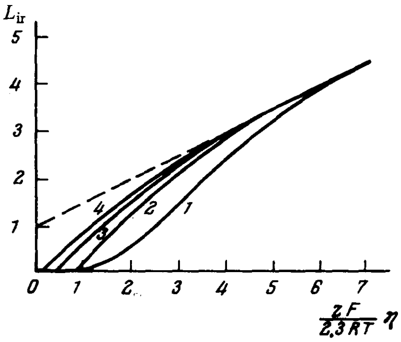

Figure 3. Variation of η with L_{ir} for a rotating mercury disc electrode corresponding to different values of j_0/c_O^0: 2) 4; 3) 1; 4) ≪ 1; β = 0.5. Curve *1* has been plotted for a stationary mercury film electrode.

For diffusion-controlled processes, the equation of the chronopotentiometric curve is

$$\eta_{\text{d}} = \frac{2.3\,RT}{zF}\left[\lg\left(1 + \frac{j_0}{c_O^0}\right) + L_O\right], \tag{21}$$

where

$$L_O = \lg\frac{\tau}{\tau - t}.$$

---

† In view of the small thickness of the mercury film electrode, the analogous Eqn. (6) is difficult to use for these purposes.

It follows from this equation that the plot of η_d against L_O is a straight line with a slope of $2.3RT/zF$. It is appropriate here to compare the equation obtained with the analogous equation [Eqn. (9)] for a stationary mercury film electrode; the evident simplicity of Eqn. (21) can be easily seen. Analysis of Eqn. (21) shows that an increase of the rate of rotation of the electrode leads to a shift of the chronopotentiometric curves towards negative potentials, the maximum shift being observed when $j_0/c_O^0 \ll 1$.

Studies at a rotating mercury disc electrode showed that the electrochemical dissolution processes for thallium and lead amalgams (in 1 M KNO_3 as the supporting electrolyte) and bismuth amalgam (in 1 M HNO_3 as the supporting electrolyte) are diffusion-controlled (Table 4). The study of the ionisation of cadmium and zinc amalgams in the appropriate supporting electrolytes at a rotating disc electrode showed that the electrochemical dissolution of these metals from the amalgams is determined by mixed kinetics (Table 6). The kinetic parameters found by the method of amalgam chronopotentiometry agree with the literature[34-38].

Table 6. The results of the study of the kinetics of the electrochemical oxidation of zinc and cadmium amalgams at a rotating mercury disc electrode ($i = 1.2 \times 10^{-4}$ A cm^{-2}, $n_{rev} = 1200$ rev min^{-1}).

Amalgam	Supporting electrolyte	$10^4 c_0^0$, M	$\frac{2.3RT}{\beta zF}$, V	βz	$10^4 i_{0_2}$, A cm^{-2}	k_S, cm s^{-1}	
						experimental data	literature data
Zn	1 *M* KNO_3	1.0	0.050	1.16	1.1	$3.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$ [36,37]
Cd	1 *M* Na_2SO_4	0.1	0.040	1.45	1.2	$1.1 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$ [38] (0.5 *M* Na_2SO_4)

It is noteworthy that the methods used in the literature[35-38] are more complex as regards apparatus and the interpretation of the results than in amalgam chronopotentiometry.

5. Analytical Scope of the Method

Using Eqn. (15), we shall estimate theoretically the minimum concentration which can be determined by the method of amalgam chronopotentiometry. When the error introduced by the capacitance current is $m\%$, we have[28,39]

$$c^0_{O,\min} = \frac{10^5 SC_d\Delta\varphi}{mzF\gamma V}\ (\text{mole litre}^{-1}), \tag{22}$$

for the film electrode and

$$c^0_{O,\min} = \frac{1{,}26 \cdot 10^6 r_0^2 C_d\Delta\varphi}{mzF\gamma V}\ (\text{mole litre}^{-1}), \tag{23}$$

for the spherical electrode, where γ is the coefficient of consumption of the solution[40,41] and V the volume of the solution analysed.

After recalculation for a sample g (in grams), we have

$$a_{\min} = \frac{AV}{10\ g} c^0_{O,\min}, \tag{24}$$

where A is the atomic weight of the element to be determined and $a_{\min}$ the minimum impurity content which can be determined.

Numerical estimates yielded $c^{0f}_{o,\min} = 6.5 \times 10^{-9}$ M, $a^f_{\min} = 6.5 \times 10^{-8}\%$, $c^{0s}_{o,\min} = 6.7 \times 10^{-9}$ M, and $a^s_{\min} = 6.7 \times 10^{-8}\%$ for the following experimental conditions: $g = 1$ g, $A = 100$, $V = 1$ ml, $\gamma = 0.63$, $C_d = 20$ μF cm^{-2}, $D_R = 2 \times 10^{-5}$ cm^2 s^{-1}, $z = 2$, $m = 5\%$, $r_0 = 4 \times 10^{-2}$ cm, $\Delta\varphi = 0.080$ V (for lead) and $S = 0.025$ cm^2 (for the film electrode). These calculations have been confirmed by experimental data obtained in studies[6,7] where lead, copper, and zinc were determined at molar concentrations of $10^{-9}n$ ($n = 4$–8).

In the analysis of multicomponent amalgams a superposition of chronopotentiograms is possible (when the equilibrium potentials of the amalgams are similar). The problem therefore arises of the resolving capacity of the method. The resolving capacity may be[28] characterised approximately by the quantity $\Delta\varphi$ (Fig. 1). The lower the value of $\Delta\varphi$ the greater the number of elements which may be determined from a single chronopotentiogram. It has been shown theoretically[28] that, for reversible processes, $\Delta\varphi$ decreases with decrease of the concentration of the depolariser ions in solution and, for irreversible processes, $\Delta\varphi$ is independent of c_O^0 (Fig. 4). Experimental investigation of the electrochemical oxidation of lead and thallium amalgams in 1 M KNO_3 supporting electrolytes (reversible processes) and zinc amalgam in 1 M KNO_3 (irreversible process) confirmed the theoretical conclusions (Fig. 4). $\Delta\varphi$ is independent of the thickness of the mercury film, which is very convenient in analytical studies (there is then no need for an accurate determination of the film thickness, which may vary during the experiments).

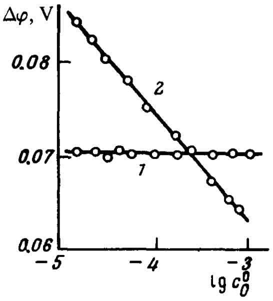

Figure 4. The influence of the depolariser concentration in solution on $\Delta\varphi$ for the electrochemical oxidation of zinc (curve *1*) and lead (curve *2*) amalgams.

The minimum value of $\Delta\varphi$ has been estimated[28] for bivalent elements, amounting to about 44 mV. For comparison, we may point out that the width of the polarographic wave for a dropping mercury electrode is about 72 mV and the width of the anodic peak in the method of amalgam polarography with accumulation is about 60 mV.

The possibility of the simultaneous determination of different elements with adequate resolution and accuracy makes the method of amalgam chronopotentiometry of potential value in analytical practise. The simplicity of the shape of the chronopotentiometric curve permits the application of the method in schemes for the automatic monitoring of continuously varying concentrations of chemical elements[42–44]. A model of a digital chronopotentiograph has been constructed for the analysis of traces of elements by amalgam chronopotentiometry[43]. Other possible designs for chronopotentiometric apparatus have been described[45–47].

The use of a rotating mercury disc electrode yields more clear-cut chronopotentiograms (Fig. 5). This is achieved as a result of the alteration of the shape of the curve (the S-shaped curve at a stationary electrode is replaced by the "logarithmic" curve at a rotating disc electrode).

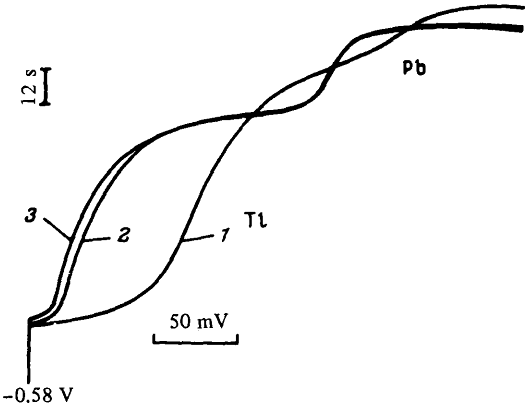

Figure 5. Chronopotentiometric curves for the ionisation of a thallium–lead amalgam at stationary (curve *1*) and rotating disc electrodes (curves *2* and *3*) for rates of rotation of 1200 and 3400 rev min^{-1} respectively.

6. Oxidation of Amalgams in the Presence of Oxygen

The interaction of the oxygen dissolved in the solution being analysed with amalgams makes a definite contribution to the dissolution of metals in the absence of a current[48]. Doronin and Kabanova[49] used the reaction of thallium amalgam with dissolved oxygen for the chronopotentiometric determination of both thallium and oxygen. The reduction of oxygen at a thallium amalgam in the absence of a current but in the presence of thallium ions in solution has been investigated[49,50].

The joint chronopotentiometric determination of thallium and oxygen is possible under certain conditions[49]. In the determination of oxygen the concentration of thallium in the amalgam should not be high, so that the rate of its dissolution in the reaction with oxygen can be measured. Preliminary electrolysis in the determination of oxygen yields the thallium amalgam and the concentration of oxygen is then found from the chronopotentiogram for the decomposition of the amalgam by the oxygen diffusion flux with the solution stirred in a specific manner. When the ratio of the concentrations of thallium and oxygen in solution is 10 : 1, oxygen can be determined at a concentration of 3×10^{-7} M or less.[49] Evidently the minimum concentration of oxygen which can be estimated is limited by the concentration of oxidants in solution, which may oxidise the metal in the amalgam to the ionic state. The possibility of determining traces of oxygen in gases or solutions by the chronopotentiometric method has also been pointed out[51].

Buffle et al.[48] examined theoretically the oxidation of metals in amalgams under chronopotentiometric conditions in the absence of a current. The following reaction then takes place at the electrode:

$$M(\mathrm{Hg}) + \frac{z}{2n}\mathrm{O}_2 \rightarrow \mathrm{M}^{z+} + \frac{z}{n}\mathrm{O}^{n-} + \mathrm{Hg}.$$

The reduction of oxygen to water (O^{2-}) or hydrogen peroxide (O^-) depends on the nature of the metal[52,53] and the experimental conditions[50].

The equations of chronopotentiometric curves have been derived under the following conditions: (1) the expression for the spreading of concentration in the mercury drop in the presence of oxygen obeys Shain's equation[54]; (2) the flux of metal to the surface of the electrode is proportional to the flux of oxygen with the sign reversed and with the proportionality coefficient $z/2n$; (3) the chemical reaction between oxygen and the amalgam is assumed to be rapid compared with diffusion, so that one can put $c^S_{O_2} = 0$; (4) the solution is stirred vigorously and the flux of oxygen (q_{O_2}) to the electrode via a diffusion layer having a thickness δ_{O_2} is

$$q_{O_2} = \frac{zD_{O_2}c^0_{O_2}}{\delta_{O_2}}. \tag{25}$$

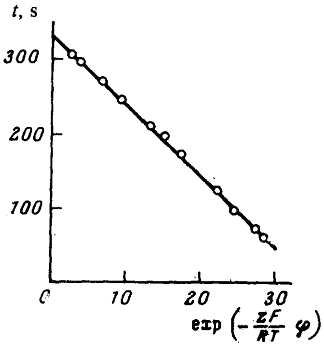

Figure 6. Relation between *t* and the potential in the electrochemical dissolution of a lead amalgam.

The equation of the chronopotentiometric curve (on the assumption that a reversible electrode process takes place) is[48]

$$\varphi = \varphi^0 + \frac{RT}{nF}\ln\left(zc^0_{O_2}\frac{D_{O_2}}{D_0}\right) - \frac{RT}{nF}\ln\left(c_R - \frac{3zc^0_{O_2}D_{O_2}t}{\delta_{O_2}r_0} - \frac{zc^0_{O_2}r_0D_{O_2}}{5D_R\delta_{O_2}} + \frac{2zc^0_{O_2}r_0}{D_R\delta_{O_2}}D_{O_2}S_{\mathrm{sph}}\right), \tag{26}$$

where

$$S_{\mathrm{sph}} = \sum_{n=1}^{\infty}\frac{\exp(-\bar{\mu}^2_n v_R)}{\bar{\mu}^2_n}.$$

Eqn. (26) was tested experimentally[43] in the oxidation of zinc, lead, and cadmium amalgams. The results of the test for lead amalgam are presented in Fig. 6 in terms of a plot of t against $\exp(-zF\varphi/RT)$. Similar results were obtained for zinc and cadmium amalgams. The value of δ_{O_2} was calculated from the slope of the plot (Fig. 6). For $D_{Pb^{2+}} = 8.3 \times 10^{-6}$ cm^2 s^{-1}, $r_0 = 0.038$ cm, and $\varphi^0 = -0.120$ V, $\delta_{O_2} = 7.5 \times 10^{-4}$ cm was obtained, which agrees approximately with the literature ($\delta_{O_2} \simeq 10^{-3}$ cm).[55]

The expression for the transition time subject to the condition $v'_R \geqslant 0.14$ is

$$\tau = \frac{\delta_{O_2} r_0 c_R^0}{3 z c_{O_2}^0 D_{O_2}} - \frac{r_0^2}{15 D_R}. \tag{27}$$

Hence it follows that the transition time is inversely proportional to the O_2 content in solution. This relation has been used[48] to determine the content of oxygen in an acetate buffer (pH 4.7). The concentration obtained $c_{O_2}^0 = 8.23 \times 10^{-7}$ M corresponds to the solubility of O_2 in the test solution.

Thus, using the reaction of dissolved oxygen with amalgams, the method of amalgam chronopotentiometry can be applied for the determination of oxygen in gases or solutions.

7. The Study of Adsorption on Mercury

The simplicity of the chronopotentiometric method in the study of the adsorption of various substances on mercury has been increasingly frequently emphasised in the literature[56-58]. A planar mercury electrode is suitable for such purposes. When the substance in the form of a sparingly soluble compound or metal deposit is adsorbed on the surface of a mercury film, the transition time characterising the complete exhaustion of both the adsorbed and non-adsorbed depolariser is described by the equation

$$\tau = \frac{zFlc_R^0}{i} + \frac{zF\Gamma}{i}, \tag{28}$$

where Γ is the amount of adsorbed substance (mole cm^{-2}).

If the electrochemically active substance is insoluble in mercury (but is adsorbed on the surface of the electrode), Eqn. (28) reduces to

$$\tau_{\text{ads}} = \frac{zF\Gamma}{i} \tag{29}$$

Using the values of τ_{ads}, it is possible to plot the adsorption isotherm. Ershler et al.[56] and Herman and Blount[59] analysed in detail various models for adsorption on mercury electrodes and the transition times. According to Herman and Blount[59], the method of chronopotentiometry with current reversal, whereby it is possible to investigate adsorption phenomena in both anodic and cathodic processes, is suitable for the study of adsorption.

8. Other Possible Applications of the Method and Some of Its Modifications

The method of amalgam chronopotentiometry can be used to determine the solubilities of sparingly soluble metals in mercury[17]. The essential feature of one of the modifications is as follows. A preliminary electrolysis is carried out for various concentrations of the element (whose solubility in solution is to be determined) during a period which is always the same and chronopotentiograms are recorded in each case. The transition time increases with increase in concentration up to a limit and then remains unchanged. This limiting transition time corresponds to the solubility of the metal in mercury. The above method yields correct results only when the solid phase formed dissolves at an infinitesimally low rate.

The above method can also be used to investigate chemical processes[60] which complicate the electrode process involving the dissolution of the amalgam (the formation of intermetallic compounds, complex formation). This problem is discussed in greater detail in the next section.

Using the method of the rotating disc electrode, it is possible to investigate the corrosion of amalgams under chronopotentiometric conditions.

An interesting version of amalgam chronopotentiometry—chronopotentiometry in the absence of a current or chronopotentiometry with a specified resistance—has been proposed[61-64]. In this method the electrochemical dissolution of the amalgam is measured with the aid of additional resistances introduced into the circuit.

Amalgam chronopotentiometry in a two-sided thin-film system has been examined[65]. The author[65] showed that the theoretical relations obtained by Christensen and Anson[66] for one-sided thin-film systems can be used in conjunction with this version of the method.

V. THEORY OF THE METHOD WHEN THE ELECTRODE PROCESS IS COMPLICATED BY CHEMICAL REACTIONS

In many cases electrode processes take place in several stages. In order to understand the mechanisms of the electrode process and particularly for a correct interpretation of experimental results, it is necessary to know the characteristics of chemical reactions at the surface of the electrode and the relations governing them.

The electrochemical dissolution of the amalgam may be complicated by chemical reactions occurring in the amalgam or in the solution. Certain metals are known to form with one another intermetallic compounds soluble in mercury[67]. In the electrochemical dissolution of such an amalgam the electrode process is complicated by the dissociation of the compound in the amalgam. If the metal ions formed on electrochemical dissolution of the amalgam react chemically with the components of the electrolyte or are involved in complex formation, the electrode process is complicated by the subsequent chemical reaction. The theory of inversion amalgam chronopotentiometry with kinetic complications has been largely described[14-16]. It is assumed that, in the presence of an excess of an indifferent electrolyte in solution, there are no adsorption effects, and that the electrolyte solution is not stirred.

1. Preceding Chemical Reactions

If the electrochemical dissolution of the amalgam is preceded by a chemical reaction (dissociation of the intermetallic compound), the electrode process can be represented schematically as follows[68,69]:

$$\mathrm{Y\,(Hg)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{M(Hg)} \;+\; n\mathrm{M_1\,(Hg)} \xrightarrow{ze} \mathrm{M}^{z+},$$

where Y is the intermetallic compound soluble in mercury and M and M_1 are the metal atoms into which the substance Y dissociates. It is postulated that Y and M_1 are not oxidised at the potential of the electrochemical oxidation of M.

The expression for the distribution of the metal concentration at the surface of an electrode of any shape, subject to the condition $D_R = I_Y = D$, is

$$c_R^S = \frac{c_R^0 - j(S_1 + K_pS_2)}{1 + K_p}. \tag{30}$$

We have for the mercury film electrode ($v_R \geqslant 0.34$)

$$S_1 = v_R + \frac{1}{3}, \tag{31}$$

$$S_2 = \frac{1}{\sqrt{K}\tanh\sqrt{K}} - \frac{e^{-Kv_R}}{K}, \tag{32}$$

and for the spherical mercury electrode ($v_R \geqslant 0.14$)

$$S_1 = v_R + \frac{1}{15}, \tag{33}$$

$$S_2 = \frac{1}{3\sqrt{K}\coth\sqrt{K} - 1} - \frac{e^{-Kv_R}}{K}, \tag{34}$$

where $K = \lambda_1 + \lambda_2$, $\lambda_1 = K_1y^2/D$, $\lambda_2 = K_2y^2/D$, and K_p is the equilibrium constant for the chemical reaction. Hence we have the following expression for the transition time subject to the condition $c_R^S = 0$:

$$v'_K = v'_R - K_pS_2(v'_K), \tag{35}$$

where v'_R corresponds to the transition time in the limiting case where the chemical reaction is fast:

$$v'_R = \frac{c_R^0}{j} - \frac{1}{3};\; v'_K = \frac{D\tau}{l^2}.$$

It follows from Eqn. (35) that the kinetic effect may be observed[69] under the condition

$$K_pS_2(v'_K) \geqslant 0.1\, v'_K. \tag{36}$$

According to Eqn. (35), when account is taken of Eqn. (32) or (34), the plot of the relation is linear with the slope at low current densities

$$\frac{K_p}{\sqrt{K}\tanh\sqrt{K}}$$

for the mercury film electrode and

$$\frac{K_p}{3\sqrt{K}\coth\sqrt{K} - 1}$$

for the spherical mercury electrode. The value of K may be calculated from these relations when K_p is known. Since v'_K is proportional to concentration for constant j, the linear plot of v'_K against concentration may be extrapolated to $v'_K = 0$. S_2 may be determined from the intercept on the ordinate axis and K_p and K can then be calculated.

In order to derive the equations of chronopotentiometric curves, it is necessary to substitute in the kinetic equation the expressions for c_R^S and c_O^S. The formula for the distribution of the concentration c_O^S has been published[1]. The equations of chronopotentiograms are simpler[68,69] when $D_O = D_R$:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln\frac{c_R^0 - jS_1 + K_pS_2}{(1 + K_p)\,c_O^S} \tag{37}$$

for reversible electrode processes, and

$$\varphi = \varphi^0 + \frac{RT}{\beta zF}\ln\frac{q}{k_S} - \frac{RT}{\beta zF}\ln\frac{c_R^0 - j(S_1 + K_rS_2)}{1 + K_p} \tag{38}$$

for irreversible electrode processes. The quantity $jK_pS_2/(1 + K_p)$ introduces a correction for the kinetic effect. Since $jK_pS_2/(1 + K_p) > 0$, the chronopotentiometric curve should shift towards positive potentials when there is a preceding chemical reaction.

2. Subsequent Chemical Reactions

The influence of the chemical reaction which follows electron transfer is manifested in processes with a reversible electrochemical stage. In irreversible processes the subsequent chemical reaction cannot have any influence on the kinetics of the electrode process. Therefore the occurrence of the subsequent chemical reaction can affect only the distribution of the metal concentration in solution. For the mechanism under consideration,

$$M(Hg) \overset{ze^-}{\rightleftarrows} M^{z+} + N \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y,$$

where M is the metal in the amalgam, M^{Z+} the metal ions formed on electrochemical dissolution of the amalgam and then reacting with the excess of the substance N, and Y the substance formed as a result of the chemical reaction (Y is not reduced or oxidised in the potential range where M is oxidised), the equation of the chronopotentiometric curve corresponding to reversible electrode processes at a mercury film electrode is (subject to the conditions $v_R \geqslant 0.34$ and $D_I = D_O = D$)[14,70]

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) + \frac{RT}{zF}\ln P(v), \tag{39}$$

where

$$P(v) = \frac{1}{1 + K_p}\left(\frac{2v^{1/2}}{\pi^{1/2}} + \frac{K_p\,\mathrm{erf}\sqrt{Kv}}{\sqrt{K}}\right). \tag{40}$$

For a fairly long transition time (low current density), the second term in Eqn. (40) becomes negligibly small compared with the first. Under these conditions, K_p may be calculated from the chronopotentiometric half-wave potential (the case of a stable equilibrium in the chemical reaction).

Using Eqn. (40), it is then possible to calculate K and hence k_1 and k_2.

The quantity $K_p\,\mathrm{erf}\sqrt{Kv}/\sqrt{K}$ introduces a correction for the kinetic effect. Since it is positive, in the subsequent chemical reaction the chronopotentiometric curve shifts towards negative potentials:

$$\Delta\varphi_{\tau/2} = \varphi_{\tau/2,K} - \varphi_{\tau/2} = \frac{RT}{zF}\ln\frac{1}{1 + K_p}\left(1 + \frac{\pi^{1/2}K_p}{\sqrt{2Kv'}}\,\mathrm{erf}\sqrt{\frac{Kv'}{2}}\right) \tag{41}$$

or in the limiting case (low current densities) we have

$$-\Delta\varphi_{\tau/2} = \frac{RT}{zF}\ln(1 + K_p). \tag{42}$$

Thus the shift of the chronopotentiometric half-wave potential, in which the current density becomes constant, does not change on further decrease of current density. Under this condition, it is fairly easy to calculate the equilibrium constant K_p.

At high current densities (low values of τ) the kinetic effect is vanishingly small and in this case Eqn. (39) assumes the form corresponding to the absence of kinetic complications.

For an irreversible chemical reaction, which occurs, for example, in the formation of many complexes, the equation of the chronopotentiogram simplifies[70]:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) + \frac{RT}{zF}\ln\frac{\mathrm{erf}\sqrt{k_1v}}{\sqrt{k_1}}. \tag{43}$$

If the rate of the chemical reaction is fairly high, we obtain the following expression from Eqn. (43) when $\sqrt{k_1 v} \geqslant 3$:

$$\varphi = \varphi_{1/2} - \frac{RT}{zF}\ln(v' - v) - \frac{RT}{2\,zF}\ln k_1, \tag{44}$$

i.e. the electrode process becomes irreversible. k_1 may be determined by Eqn. (44) from the chronopotentiometric half-wave potential.

By analysing the $\varphi - t$ curves, Bakanov[14] derived the following criterion of the irreversibility of the electrode process followed by a chemical reaction:

$$k_f \ll \frac{v'\sqrt{k_1}}{\operatorname{erf}\sqrt{k_1 v'}}. \tag{45}$$

Thus, when the rate constant for the chemical reaction k_1 is greater than k_f (k_f is the formal rate constant for the cathodic process), the electrode process becomes irreversible. This conclusion is consistent with the above hypothesis that the process is irreversible.

The equations of chronopotentiometric curves for a spherical mercury electrode are more complex. They have been analysed in detail together with a quasireversible electrode process for electrodes of both types[14,70].

Table 7. Criteria for the determination of kinetic mechanisms.

Kinetic mechanism	Logarithmic time function	Slope of linear section*	$i\tau$	$\Delta\varphi_{\tau/2,\,K}$
1) $M(Hg) \rightleftarrows M^{z+} + ze$	$\frac{\tau}{\tau - t}\left(1 + \frac{2qt^{1/2}}{\pi^{1/2}D_o^{1/2}C_o^0}\right)$	$\frac{RT}{zF}$	const	0
2) $M(Hg) \rightarrow M^{z+} + ze$	$\frac{\tau}{\tau - t}$	$\frac{RT}{\beta zF}$	const	0
3) $Y(Hg) \underset{k_2}{\overset{k_1}{\rightleftarrows}} M + nM_1 \rightleftarrows M^{z+} + ze$	$\frac{v' - v + K_p(S_2' - S_1)}{\frac{c_0^0}{j} + \frac{2}{\pi^{1/2}}v^{1/2}}$	$\frac{RT}{zF}$	f (*i*)	>0
4) $Y(Hg) \underset{k_2}{\overset{k_1}{\rightleftarrows}} M + nM_1 \rightarrow M^{z+} + ze$	$v' - v + K_p(S_2' - S_2)$	$\frac{RT}{\beta zF}$	f (*i*)	>0
5) $M(Hg) \rightleftarrows M^{z+} + ze + N \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y$	$\frac{S(v)}{v' - v}$	$\frac{RT}{zF}$	const	<0
6) $M(Hg) \rightleftarrows M^{z+} + ze + N \xrightarrow{k_1} Y$	$\frac{\operatorname{erf}\sqrt{k_1 v}}{v' - v}$	$\frac{RT}{zF}$	const	<0

---

* The slope of the linear section is found from the time variation of the overvoltage.

3. Criteria for the Determination of Kinetic Complications in Amalgam Chronopotentiometry

Analysis of the transition times and of the time variation of the potential makes it possible to determine the kinetic mechanisms of electrode processes. If the electrochemical amalgam dissolution stage is preceded by a chemical stage, the quantity $i\tau$ depends on the current density and the kinetic parameters may be determined from the transition times. Indeed, we can put Eqn. (35) in the form

$$v_R' = \frac{c_R^0}{j} - K_p S_2(v_R') - b, \tag{46}$$

where $b = 1/3$ for the mercury film electrode and $b = 1/15$ for the spherical mercury electrode. It follows from Eqn. (46) that

$$jv_R' = c_R^0 - j\,[K_p S_2(v_R') + b], \tag{47}$$

whence it is seen that the product jv_R' depends on the current density; for short transition times, this relation is non-linear.

When the amalgam ionisation stage is followed by a chemical reaction and the preceding stage is merely diffusion in the amalgam, the product $i\tau$ is independent of current density, as in the absence of chemical reactions. Therefore in such cases the potential–time curves must be analysed in order to obtain kinetic data. The following criteria for the determination of kinetic mechanisms may be suggested: (1) a linear relation between the logarithm of the corresponding time function and potential; (2) dependence of the product $i\tau$ on current density; (3) a change in the half-wave potential of the chronopotentiometric curve $\Delta\varphi_{\tau/2}$ in the presence of kinetic complications. Table 7 illustrates the application of these criteria to certain electrode processes occurring in the electrochemical dissolution of amalgams at a mercury film electrode. All the relations indicated in Table 7 were analysed above in detail.

4. Application of Amalgam Chronopotentiometry in the Study of Complexes Formed During the Electrochemical Dissolution of Amalgams

The problems of inversion amalgam chronopotentiometry in relation to electrode processes complicated by complex formation have been examined[14,15,71-74]. If a reversible process takes place at the electrode with formation of equilibrium complexes in the presence of an excess of the ligand, then the composition and stability constant of the complex are determined from the dependence of the shift of the chronopotentiometric half-wave potential on ligand concentration[14]. The shift of the half-wave potential is described by the following equation on the assumption that the ligand concentrations at the electrode surface and in the bulk of the electrolyte are the same[75]

$$\Delta\varphi_{\tau/2,k} = -\frac{RT}{zF}\ln\sum_{n=0}^{p} K_n (c_X)^n, \tag{48}$$

where K_n is the stability constant of the nth complex and c_X is the ligand concentration.

Since the dependence of $\varphi_{\tau/2,k}$ on $\lg c_X$ is similar to that in the polarographic method, Eqn. (48) can be analysed by the method of de Ford and Hume[76].

When only one type of complex is present in solution, Eqn. (48) reduces to

$$\Delta\varphi_{\tau/2,k} = -\frac{RT}{zF}\ln K_n - \frac{nRT}{zF}\ln c_X. \tag{49}$$

According to this expression, the dependence of the chronopotentiometric half-wave potential on the logarithm of ligand concentration should be linear; the coordination number n may be determined from the slope of this relation and the stability constant K_n may be found from the intercept on the ordinate axis, where $c_X = 0$.

Complex formation in the presence of concentration polarisation with respect to the ligand has been examined[74]. As in the presence of an excess of the ligand, the quantity $\Delta\varphi_{\tau/2,k}$ is in this case defined by Eqn. (49).

Bakanov[14] and Bakanov and Zakharov[71] tested the theoretical conclusions in relation to the hydroxo- and chloro-complexes formed in the electrochemical oxidation of lead and cadmium amalgams respectively. The ionic strength of the solution was kept constant and equal to unity by varying the concentration of KNO_3. The concentration of lead ions in solution was 1×10^{-4} M. The experiments were performed at a mercury film electrode. It was established that in 1 M KOH as the supporting electrolyte lead forms the complex $Pb(OH)_3^-$. The slope of the relation between $\Delta\varphi_{\tau/2,k}$ and c_{OH^-} proved to be 85.5 mV. $\lg K_n = 12.55$ was found from the intercept on the ordinate axis. The results agree well with those obtained in other studies[77-79]. Lingane[80] obtained $\lg K_n = 12.8$ and $n = 3$ at an ionic strength of 0.1.

In the electrochemical dissolution of a cadmium amalgam in 1 M ($KCl + KNO_3$) as the supporting electrolyte the complexes $CdCl^+$ and $CdCl_2$ are formed in succession[14]. Their stability constants were found to be 21.5 and 60.7 respectively, in good agreement with other results[79,80].

The method of amalgam chronopotentiometry has been applied[15,72] in the study of the kinetics of the electrochemical dissolution of the amalgam with participation of complex ions. The following mechanism was proposed:

$$z_R M(Hg) + p_2 X \rightarrow z_O MX_{p_2} + ze$$

with the subsequent attainment of the equilibrium

$$z_O MX_{p_2}^{(p_2 m-z)-} + (p - p_2)\, X^{m-} \rightleftarrows z_O MX_p^{(pm-z)-},$$

where P is the composition of the complex predominating in the solution, p_2 the composition of the intermediate complex formed directly in the electrochemical dissolution of the amalgam, z_O and z_R are the orders of the electrochemical reaction with respect to the oxidant and reductant respectively, and X is the ligand.

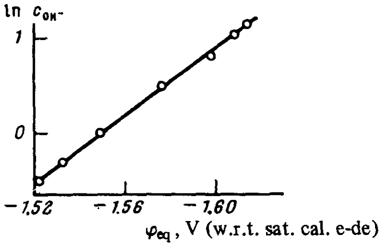

Figure 7. The dependence of the equilibrium potential of a zinc amalgam on OH^- concentration.

The general case has been analysed[15] on the hypothesis that a quasireversible electrode process takes place with subsequent complex formation. It was shown that the composition of the intermediate complex p_2 and the order of the electrochemical reaction may be determined from the exchange current density by means of the following relations:

$$\frac{\partial \ln i_O}{\partial \ln c_R^0} = \alpha z_R - \beta; \quad \frac{\partial \ln i_O}{\partial \ln c_O^0} = \beta z_O - \alpha: \qquad (50)$$
$$\frac{\partial \ln i_O}{\partial \ln c_X} = p_2 - \beta p.$$

The conclusions reached were tested in relation to the formation of zinc hydroxide and tartrate complexes formed in the electrochemical dissolution of a zinc amalgam[72]. The ionic strength was maintained at 3 by adding NaCl solution. The zinc hydroxide complexes were studied in a solution having the composition x M KOH + $(3 - x)$ M NaCl. To determine the composition of the complex predominating in solution, a study was made of the dependence of the equilibrium potential on the concentration of OH^- ions for a constant zinc concentration in solution and in the amalgam (Fig. 7). The slope of this relation pRT/zF proved to be 0.057, whence $p = 4$ ($z = 2$), in agreement with Vetter's data[81]. The values of i_O, z_R, and βz were determined from a plot of η against L_{ir} (Fig. 8): $i_O^0 = (1.75 \pm 0.3) \times 10^{-2}$; $\beta z = 0.48 \pm 0.02$; $z_R = 0.89 \simeq 1.0$. Here i_O^0 is the standard exchange current density. Using Fig. 7 and Eqns. (50), the composition of the complex $p_2 = 0.96 \simeq 1$ was determined. On the basis of the results, the ionisation of zinc amalgam can be represented as follows:

$$Zn(Hg) + OH^- \rightarrow Zn(OH)^+ + 2e + Hg,$$
$$Zn(OH)^+ + 3\,OH^- \rightleftarrows [Zn(OH)_4]^{2-}.$$

The conclusions reached agree well with the literature data[81].

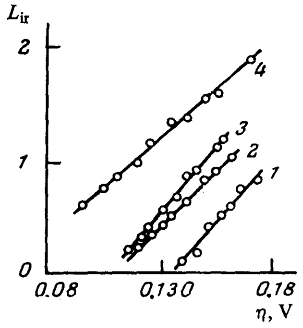

Figure 8. Variation of L_{ir} with $\eta_{Zn(Hg),Zn^{2+}}$ at different zinc amalgam concentrations (g-atom litre^{-1}): 1) 6.1×10^{-3}; 2) 1.3×10^{-2}; 3) 3.6×10^{-2}; 4) 5×10^{-2}.

Similar studies on zinc tartrate complexes showed that, in agreement with the literature[82], the complex Zn(tart) predominates in solution. It was established that $z_R = 1.0$, $\beta = 0.49 \pm 0.02$, $i_O^0 = (2.55 \pm 0.33) \times 10^{-2}$, and $p_2 = 0.13$. The value of p_0 obtained leads to the conclusion that mainly hydrated zinc ions are involved in the ionisation of the amalgam.

The results quoted above have shown that the method of amalgam chronopotentiometry can be used to investigate complex formation.

5. Simultaneous Chemical Reactions in Amalgam Chronopotentiometry

When several electrochemically active substances whose standard potentials differ appreciably are present jointly in solution, a simultaneous amalgam oxidation reaction may occur. Chemical oxidation of the amalgam in the presence of oxygen has been investigated[7,83,84].

A quantitative treatment of this phenomenon for the spherical mercury electrode was described for the first time by Barański and Galus[85]. The authors began with the following mechanism:

$$M_1\,(Hg) \rightleftarrows M_1^{z_1+} + z_1e$$
$$z_2M_1\,(Hg) + z_1Ox_2 \rightarrow z_2M_1^{z_1+} + z_1R_2,$$

where Ox_2 is the oxidised form of the reactant (it may consist either of the ions of a metal more electropositive than M_1 or of traces of dissolved oxygen) and R_2 is the reduced form of the reactant.

The electrode reaction is assumed to be reversible. If the rate of the chemical reaction is limited by the diffusion of Ox_2, the expression for the concentration can be obtained from the equation of Fick's Second Law. The quantitative treatment of the influence of the simultaneous chemical reaction on the electrode process involving the electrochemical dissolution of the amalgam was based by the authors[85] on the equality

$$i_0 = i + i_c,$$

where i_0 is the overall current in the circuit, i the electrode reaction current, and i_C the amalgam chemical oxidation current. The results of the study are expressed as the ratios of the transition times:

$$\frac{\tau_0}{\tau} = \frac{15\,D_{R_1}\tau_0}{15\,D_{R_1}\tau_0 + r_0^2} - \frac{6\,D_2^{1/2}z_2c_2^0}{\pi^{1/2}z_1r_0c_{R_1}^0}\tau_0^{1/2} - \frac{3\,z_2D_2c_2^0}{z_1r_0^2c_{R_1}^0}\tau_0, \qquad (51)$$

where τ_0 is the experimental transition time, τ the transition time in the absence of a chemical reaction, and c_2^O the initial concentration of Ox_2.

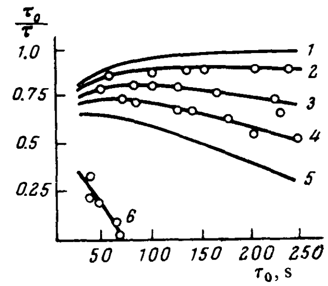

Figure 9. Theoretical $\tau_0/\tau - \tau_0$ relations for different values of $c_2^0/c_{R_1}^0$: 1) 0; 2) 0.013; 3) 0.04; 4) 0.067; 5) 0.1; 6) 0.33. The circles represent experimental data. Experimental conditions: 0.1 M KCl supporting electrolyte; $c^0_{Zn^{2+}} = 1.7 \times 10^{-5}$ M; $c^0_{Cd^{2+}} = 1.6 \times 10^{-5}$ (curves *2–4*); $c^0_{Cd^{2+}} = 1.6 \times 10^{-4}$ (curve *6*).

Fig. 9 presents curves calculated by Eqn. (51) for the following parameters: $r_0 = 0.043$ cm; $D_{R_1} = 2 \times 10^{-5}$ cm^2 s^{-1}; $D_2 = 7.9 \times 10^{-6}$ cm^2 s^{-1}; $z_1 = z_2$.

It follows from Eqn. (6) that, when $i \rightarrow 0$, then $\tau \rightarrow \infty$; however, owing to the chemical oxidation of the amalgam, in practise the transition time is always finite and equal to τ_C; it can be obtained from Eqn. (51) subject to the condition $\tau_0/\tau = 0$ (or can be found graphically). For example, when $c_2^0/c_{R_1}^0 = 0.33$, then $\tau_C = 70$ s, i.e. is equal to the maximum transition time in the chemical oxidation of the amalgam. When $c_2^0/c_{R_1}^0 \leq 0.01$, the error in the determination of the transition time due to the chemical oxidation of the amalgam may be neglected.

The experimental results obtained in the study of the electrochemical oxidation of a zinc amalgam in the presence of Cd^{2+} ions in solution are presented in Fig. 9 in the form of circles. Those on curves *2–4* and *6* correspond to different durations of preliminary electrolysis (240, 80, 40, and 90 s respectively). The satisfactory agreement between the experimental and theoretical curves is noteworthy.

Barański and Galus[85] described two methods of reducing the corrosion of amalgams in the presence of various impurities in solution: (1) by adding surface-active substances (which complicates the theoretical interpretation of the results) and (2) by additional preliminary electrolysis in an unstirred solution. A "diffusion barrier" is then created for Ox_2, as a result of which its concentration at the electrode surface falls. This procedure has been used[86] in a study of a multicomponent system under chronopotentiometric conditions.

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Electrophilic Amination†

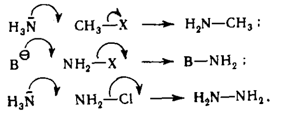
E.Schmitz

The review is devoted to reactions in which amino-, alkylamino- and acylamino-groups are transferred to nucleophilic agents. Electrophilic aminating agents are chloramine, hydroxylamine-*O*-sulphonic acid, oxaziridines unsubstituted at the nitrogen atom, and *N*-acyloxaziridines. The formation of three-membered rings with two heteroatoms, occurring as intramolecular electrophilic amination, is discussed.
The bibliography includes 99 references.

CONTENTS

I. INTRODUCTION

The majority of the reactions with the aid of which amino-nitrogen is introduced into molecules proceed as nucleophilic substitutions. The nucleophilic agent is ammonia or an amine, which substitutes another group, for example, in the interaction of ammonia with alkyl halides [reaction (1)]. These reactions have been known for a long time, have been thoroughly investigated, and are therefore not considered in this review.



(1)
(2)
(3)

Substitution reactions in which nitrogen-containing compounds behave as electrophilic agents are encountered more rarely. In these reactions [see Eqn. (2), which formulates the general case involving a base B^-] the nitrogen is linked to a group which is substituted in the course of the reaction by a nucleophilic agent. The Raschig synthesis of hydrazine [reaction (3)], in which chloramine aminates an ammonia molecule via an electrophilic mechanism[1], is a prototype of reactions of this kind. Together with chloramine, hydroxylamine-*O*-sulphonic acid later came to be used as an aminating agent[2]. The ability of certain oxaziridines to transfer NH and NCOR groups has been discovered in recent years[3]. Reactions of compounds of this type are very similar and are treated in this review as electrophilic amination. The reactions involving transfer of nitrogen-containing groups in which the intermediate formation of nitrenes has been firmly established or postulated are not discussed. A number of reviews have been devoted to such reactions[4-7]. Reactions in which the intermediate stage proceeds via the solvolysis of chloramines, nitrenium ions, and cations with an electron sextet are likewise disregarded[8].

II. REACTIONS OF CHLORAMINE AND SUBSTITUTED CHLORAMINES

An example of electrophilic amination with the aid of chloramine which has been known for a long time and has been most thoroughly investigated is the Raschig synthesis of hydrazine[1]. It has been firmly established that, in contrast to frequently expressed hypotheses, 1,1-elimination from chloramine followed by the interaction of NH with ammonia does not occur and there is instead a synchronous dissociation of the N−Cl bond and the formation of the N−N bond [see Eqn. (3)][9].

The role of the base in the initial method for the synthesis of hydrazine can be accounted for by partial deprotonation to give the chloramide anion. Thus the formation of hydrazine should be regarded as electrophilic amination in which chloramine and the chloramide anion behave as competing electrophilic agents:

$$\begin{array}{l} NH_2-Cl \xrightarrow{NH_3} H_2N-NH_2 \\ \quad\uparrow\downarrow \\ {}^{\ominus}NH-Cl \xrightarrow{NH_3} H_2N-NH_2\,. \end{array} \qquad (4)$$

Later studies of the interaction of chloramine with primary[10], secondary[11], and tertiary[12] amines showed that the presence of a strong base is not a precondition for the formation of the N−N bond: the majority of studies on the synthesis of alkylhydrazines have been carried out with chloramine–ammonia mixtures, obtained by the gas-phase chlorination of ammonia, which were combined with amines without adding a strong base. It has been shown[13] that the amination of tertiary amines by chloramine follows second-order kinetics. The ratios of the rates of interaction of ammonia, n-propylamine, and di-n-propylamine with chloramine are 1 : 140 : 460.[14]

The interactions of chloramine with the most important classes of nucleophilic agents and their anions have been studied in the last 20 years. In base-catalysed amination 2-pyridone gives rise to 1-aminopyridone (I);[15] on interaction with chloramine, *NN*-dialkylhydrazines form triazanium salts (II).[16,17] Phosphites give rise to aminophosphonium chlorides (III),[18] triphenylarsine and stibines are converted into arsonium and stibonium salts (IV) and

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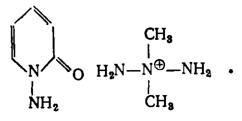
† Translated into Russian from German by T.A. Burtseva and retranslated into English.

(V),[20] while aminosulphinium salts (VI) are formed from thioethers[21].



(I) (II)

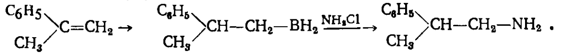
On treatment with an excess of chloramine, the latter are capable of combining with a second NH group[22,23].

$H_2N{-}P^{\oplus}(n\text{-}Bu)_3Cl^{\ominus}$ (III) $H_2N{-}As^{\oplus}(C_6H_5)_3Cl^{\ominus}$ (IV)

$H_2N{-}Sb^{\oplus}R_3Cl^{\ominus}$ (V) $H_2N{-}S^{\oplus}R_2X^{\ominus}$ (VI) .

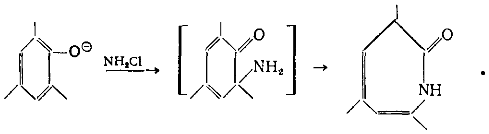
Relatively little is known about amination at a carbon atom. The interaction of chloramine with a Grignard reagent[24], which makes it possible, for example, to obtain a good yield of benzylamine from benzylmagnesium chloride [Eqn. (5)], was achieved comparatively long ago. Subsequently chloramine was used to convert into amines, via reaction (6), the products of the hydroboration of olefins[25]:

$$C_6H_5{-}CH_2{-}MgCl \xrightarrow{NH_2Cl} C_6H_5{-}CH_2{-}NH_2\ , \tag{5}$$



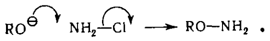
$$(C_6H_5)(CH_3)C{=}CH_2 \rightarrow (C_6H_5)(CH_3)CH{-}CH_2{-}BH_2 \xrightarrow{NH_2Cl} (C_6H_5)(CH_3)CH{-}CH_2{-}NH_2\ . \tag{6}$$

When polyalkylphenols react with chloramine, amination at the oxygen atom does not occur, as believed previously; instead, the ring is expanded to give a lactam in which the first stage must be regarded as *C*-amination[26]:



(7)

On the other hand, *O*-amination is possible for alkoxides and it has been suggested for the synthesis of *O*-alkylhydroxylamines[27]:

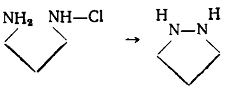


$$RO^{\ominus}\ NH_2{-}Cl \longrightarrow RO{-}NH_2\ . \tag{8}$$

We may also recall the interaction of chloramine with oximes to form diazo-compounds, which was known previously only for a diketomonoxime[28], was later extended to simpler ketoximes[20], and was used finally to synthesise diazomethane [Eqn. (9)]:[30]

$$R_2C{=}NOH \xrightarrow{NH_2Cl} R_2\overset{\ominus}{C}{-}\overset{\oplus}{N}{\equiv}N\ . \tag{9}$$

Analysis of the extensive literature on chloramine leads to the striking observation that only a few reactions of chloramine can be extended to *N*-chloroalkylamines. The formation of the N–N bond between the amine and *N*-chloroalkylamine can be achieved only with simultaneous ring closure[31]:



(10)

The interaction of *N*-chloroalkylamines, RNHCl, and *N*-chlorodialkylamines, R_2NCl, via the electrophilic amination mechanism has been described only for powerful nucleophilic agents, in particular for sulphur- and phosphorus-containing compounds. For example, chloramine reacts with mercaptides to form sulphenamides[32]:

$$R'{-}S^{\ominus} + R{-}NH{-}Cl \rightarrow R'{-}S{-}NH{-}R\ . \tag{11}$$

Thiocyanate is aminated by reaction with *N*-chlorodialkylamines to form *N*-thiocyanatoamines[33]:

$$^{\ominus}SCN + (CH_3)_2N{-}Cl \rightarrow (CH_3)_2N{-}SCN\ . \tag{12}$$

Tri(hydroxymethyl)phosphine reacts with *N*-chlorodimethylamine to form the N–P bond[34]:

$$(HOCH_2)_3P + (CH_3)_2N{-}Cl \rightarrow (CH_3)_2N{-}P^{\oplus}(CH_2OH)_3\ . \tag{13}$$

The amination of azide ions to give substituted aminoazides has been reported[33]. The amination of Grignard reagents by *N*-chloroalkylamines is possible[35].

Reactions of chloramine via the electrophilic amination mechanism take place also in the alkaline cleavage of chloramine to nitrogen and ammonia, which has been known for a long time. It has been shown that hydroxylamine is formed in the first stage [Eqn. (14)][36] and this is followed by the electrophilic amination of hydroxylamine to diimide [reaction (15)]. The formation of diimide is confirmed by the powerful hydrogenating effect in the decomposition of chloramine in alkaline solutions; for example, cinnamic acid is hydrogenated under these conditions of hydrocinnamic acid[37]:

$$HO^{\ominus} + NH_2Cl \rightarrow HO{-}NH_2\ , \tag{14}$$

$$HO{-}NH_2 + NH_2Cl \rightarrow [HO{-}NH{-}NH_2] \rightarrow HN{=}NH\ , \tag{15}$$

$$2\,HN{=}NH \rightarrow N_2 + N_2H_4\ , \tag{16}$$

$$N_2H_4 + NH_2Cl \rightarrow HN{=}NH + NH_3\ , \tag{17}$$

$$\overline{3\,NH_2Cl \rightarrow N_2 + NH_3\ .} \tag{18}$$

Bearing in mind that, on disproportionation, two diimide molecules form nitrogen and hydrazine and that the latter may be oxidised to diimide, which requires the consumption of yet another chloramine molecule, it is possible to obtain a sequence of reactions [reactions (14)–(17)], which reflects the overall formation of nitrogen and ammonia from three chloramine molecules [Eqn. (18)].

The alkaline decomposition of dichloramine, in which two molecules of the latter decompose with formation of nitrogen, chlorite, and hypochlorite, has been studied recently[38]:

$$2\,NHCl_2 + 4\ {}^{\ominus}OH \rightarrow N_2 + 3\,Cl^{\ominus} + ClO^{\ominus}\ . \tag{19}$$

The pronounced chlorinating effect on substrates, subjected to the action of radicals (for example ethyl ether or cyclohexene), observed in the decomposition of dichloramine in alkaline media, permitted the conclusion that the reaction begins with electrophilic amination and the formation of trichlorohydrazine. The elimination step then results in the formation of dichlorodiimide, which is regarded as a source of atomic chlorine:

$$2\,NHCl_2 \rightarrow Cl_2N{-}NH{-}Cl \rightarrow Cl{-}N{=}N{-}Cl \rightarrow N_2 + 2\,Cl^{\cdot}\ . \tag{20}$$

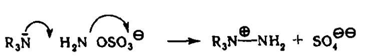
The reactions with *N*-halogenoamines have been recently discussed by Kovacic et al.[39]

III. REACTIONS OF HYDROXYLAMINE-*O*-SULPHONIC ACID AND *O*-ACYL DERIVATIVES OF HYDROXYLAMINE

Another widely used aminating agent is hydroxylamine-*O*-sulphonic acid (HSA). It was obtained for the first time by Sommer and coworkers[2,40], who also discovered the ability of HSA to convert primary and secondary aliphatic and aromatic amines into hydrazines.

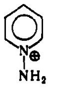
It follows from the data of these investigators, who later studied the preparative use of HSA, that the rate of reaction depends on the nature of the compound aminated. For example, secondary amines react with HSA at 0°C in the course of several hours and tertiary amines react in a few minutes[41]. Evidently, the nucleophilic agent is involved in the rate-limiting stage of the reaction.

The preliminary decomposition of HSA to NH and sulphate, which has been sometimes suggested, is therefore unlikely. Furthermore, it has been shown that the reversible decomposition to NH and sulphate does not occur either: partial decomposition of HSA in dilute NaOH solution in the presence of labelled sulphate does not result in the formation of radioactive HSA.[42] Therefore, an electrophilic mechanism in which a new linkage is formed and sulphate is displaced synchronously, must be adopted for all amination reactions with the aid of HSA, which are faster than the decomposition of HSA in the absence of a nucleophilic agent:

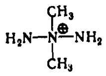


$$R_3N\; H_2N{-}OSO_3^\ominus \longrightarrow R_3\overset{\oplus}{N}{-}NH_2 + SO_4^{\ominus\ominus} \qquad (21)$$

Subsequently amination by HSA was developed into a preparative method for the synthesis of substituted hydrazines. Gever and Hayes[43] obtained ethyl-, propyl-, isopropyl-, n-butyl-, n-pentyl-, and 2-hydroxyethylhydrazines by the amination of primary amines. An excess of the amine is usually employed in order to suppress the self-decomposition of HSA in an alkaline medium and the subsequent reaction of the resulting hydrazine with HSA. Gösl and Meuwsen[41] and Sisler et al.[44] reported almost simultaneously the synthesis of hydrazine from HSA. The former investigators were able to aminate primary, secondary, and tertiary aliphatic amines to give the corresponding hydrazines. Sisler et al. aminated in accordance with Eqn.(21) tertiary aliphatic amines and dimethylaniline to form hydrazinium salts. Under suitable conditions, aniline is converted into phenylhydrazine in 80% yield[41]. Pyridine gives rise to the N-aminopyridinium cation (VII). The corresponding products are obtained from alkylpyridines and quinoline. NN'-Dimethylhydrazine is aminated to give the dimethyltriazanium cation (VIII):[45]



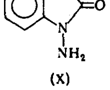
(VII)



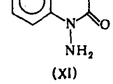
(VIII)

(IX)

The amination of aziridine to an N-amino-derivative (IX) has been described[46], but the yield is low. In certain cases an acylated nitrogen atom is sufficiently nucleophilic after deprotonation to be aminated by HSA. Thus, cyclic acid amides, for example compounds (X) and (XI), have been converted into hydrazides with the aid of HSA.[47] Evidently, simple acid amides have not, as yet, been made to undergo this type of reaction.



(X)

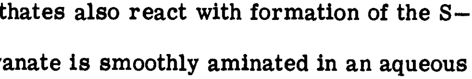


(XI)

Hydrazineisodisulphonate is obtained comparatively easily in accordance with Eqn.(22):[48]

$$HN(SO_3H)_2 \xrightarrow{KOH;\ HSA} H_2N{-}N(SO_3H)_2\,. \qquad (22)$$

In the presence of a large excess of HSA, the N-alkyl group is split off from sulphonamides in the form of a hydrocarbon. Under these conditions, N-amination probably takes place with subsequent elimination of the sulphinate residue[49]:



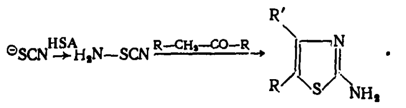
$$R{-}NH{-}SO_2{-}R' \xrightarrow{HSA} R{-}\underset{NH_2}{\underset{|}{N}}{-}SO_2{-}R' \rightarrow R{-}N{=}NH \rightarrow RH\,. \qquad (23)$$

Alkoxides react via the electrophilic amination mechanism with formation of O-alkylhydroxylamines. O-Alkylhydroxylamines have been obtained from simple C_2-C_4 alcohols and benzyl alcohol in yields of 27–49%.[50] In the presence of KOH, phenol is aminated by HSA to O-phenylhydroxylamine[51]:

$$C_6H_5{-}O^\ominus + H_2N{-}OSO_3^\ominus \rightarrow C_6H_5{-}ONH_2\,. \qquad (24)$$

Similarly to the reaction employing chloramine, triphenylphosphine and thioethers can be aminated with the aid of HSA.[52] In the latter case only one NH group adds on. Xanthates also react with formation of the S–N bond[53].

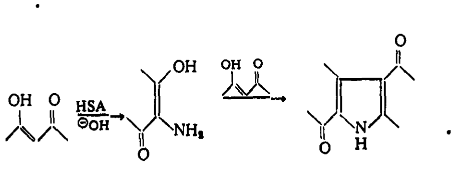
Thiocyanate is smoothly aminated in an aqueous alkaline solution. The thiocyanatoamine formed is of interest because it converts ketones into aminothiazoles in satisfactory yields[54]:



(25)

The olefin hydroboration products can be converted by the Brown reaction into amines by a treatment not only with chloramine but also with HSA.[24]

Relatively little is known about the electrophilic amination of carbanions, although in the instances described the reaction proceeds very smoothly. In dilute NaOH solution, acetylacetone reacts with HSA below room temperature in the course of several minutes. If two moles of the diketone per mole of HSA are used, the amination product condenses with the excess diketone into a pyrrole derivative[55,56]:



(26)

Acetoacetic ester derivatives also give rise to pyrrole compounds.

Hieber and Buetner[57] aminated the hydrogen tetracarbonylferrate anion:

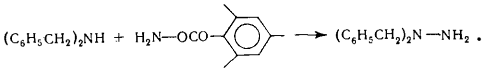
$$HFe(CO)_4^\ominus \xrightarrow{HSA} Fe(CO)_4NH_2\,. \qquad (27)$$

When the reaction with HSA, which usually takes place in aqueous alkaline solutions, is considered, account must be taken of the competing alkaline decomposition of HSA. In the case of chloramine this decomposition leads to the formation of a mole of NH_3 and N_2. This overall result [see Eqn.(32)] can also be represented by a series of amination stages [Eqns.(28)–(31)].[58] The reaction begins with the amination of the hydroxide ion; it has been shown with the aid of ^{18}O that the oxygen in the hydroxylamine produced originates from water[59]. The amination of hydroxylamine to diimide has been demonstrated by the fact that double bonds are hydrogenated both in the alkaline decomposition of HSA and in the reaction occurring in a mixture of HSA and hydroxylamine[58]:

$$\begin{array}{lr} HO^{\ominus} + HSA \rightarrow HO{-}NH_2\ , & (28) \\ HONH_2 + HSA \rightarrow HN{=}NH\ , & (29) \\ 2\,HN{=}NH \rightarrow N_2 + N_2H_4\ , & (30) \\ N_2H_4 + HSA \rightarrow H_2N{-}NH{-}NH_2{-}HN{=}NH + NH_3\ , & (31) \\ \hline 3\,HSA \rightarrow N_2 + NH_3\ . & (32) \end{array}$$

The hypothesis of the formation of triazane at an intermediate stage in reaction (31) has been proved by the fact that the reaction of [^{15}N]hydrazine with HSA results in the formation of some labelled NH_3.[58]

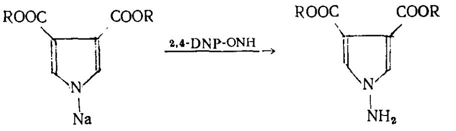
There has been no lack of attempts to discover other electrophilic aminating agents. These began with hydroxylamine containing an active group capable of being eliminated. The first studies were carried out by Carpino[60], who found that *O*-mesitoylhydroxylamine aminates dibenzylamine to dibenzylhydrazine:



(33)

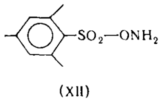
The same investigator reported later[51] the amination of carbazole to *N*-aminocarbazole (in 60% yield), of naphthalimide to *N*-aminonaphthalimide (in 81% yield), of benzylbenzamide to the corresponding hydrazine, of *N*-tosylated 1-aminomethylnaphthalene to the *N*-amino-derivative, and of t-butyliminodicarboxylate to the corresponding hydrazine derivative[62].

Sheradski[63] discovered the effective aminating activity of *O*-(2,4-dinitrophenyl)hydroxylamine. He was able to aminate in 88–95% yield sodium phthalimide, *N*-tosylbenzylamine, and pyrrole-3,4-dicarboxylate ester[63]:

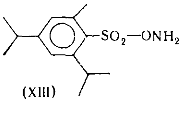


(34)

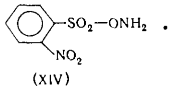
CH acids, such as methyl fluorene-9-carboxylate and diethyl phenylmalonate, are also aminated[64]. Tamura and coworkers[65–67] achieved electrophilic amination with the aid of *O*-mesitylenesulphonylhydroxylamine (XII), *O*-picrylhydroxylamine, and two other *O*-sulphonated hydroxylamines [compounds (XIII) and XIV)]:



(XII)



(XIII)

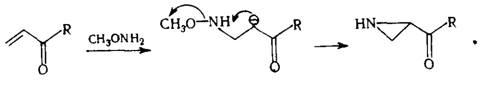


(XIV)

It proved possible to aminate tri-n-butylamine, diphenyl sulphide, diphenyl sulphoxide, triphenylphosphine, quinoline, pyridazine, pyridine, and substituted pyridines. The amination of tertiary amines takes place particularly smoothly and is used to synthesise *N*-amino-derivatives of alkaloids[68].

IV. THE SYNTHESIS OF THREE-MEMBERED RINGS WITH TWO HETEROATOMS

The formation of a new bond in electrophilic amination plays an insignificant role in the syntheses of three-membered rings with a single heteroatom. Of the large number of syntheses of aziridines, mention should be made only of the reaction of $\alpha\beta$-unsaturated ketones with *O*-alkylhydroxylamines, which may be regarded as electrophilic amination[70]:

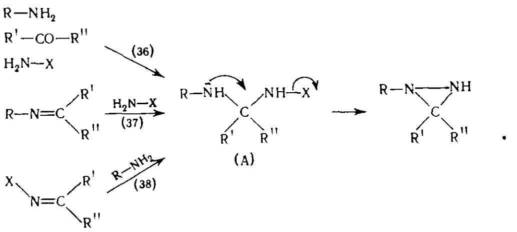


(35)

However, electrophilic amination is a dominant process in the synthesis of three-membered rings with two heteroatoms. If one disregards certain photochemical reactions, the three-membered ring is formed in this case always with the closure of the bond between the two heteroatoms. In the synthesis of diaziridines this bond is always formed as a result of electrophilic amination.

Syntheses of Diaziridines

Numerous versions of the synthesis of $\overline{C-N-N}$ rings are known. It proceeds as the reaction between a carbonyl compound, an amine, and an aminating agent, and it is frequently immaterial whether all three reactants are made to react simultaneously [Eqn.(36)], or whether the carbonyl compound and the amine form initially a Schiff base which then reacts with the aminating agent [Eqn.(37)], or whether the product of the condensation of the carbonyl compound and the aminating agent is made to react with the amine [Eqn.(38)]. Ring closure via the geminal stage (A) is an intramolecular analogue of the Raschig hydrazine synthesis.

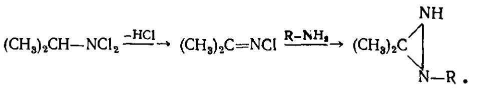


The synthesis of diaziridines with three substituents R, R′, and R″ is restricted to aliphatic compounds but is of general importance in this field. The nitrogen of the aminating agent can also carry an additional alkyl group.

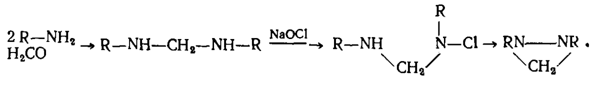
The following versions of the synthesis of diaziridines, which usually takes place with satisfactory yields, have been described.

1. Ketone + NH_3 + $ClNH_2$. In this process ammonia is subjected to gas-phase chlorination and is made to react with acetone[71] or a stream of NH_3 + $ClNH_2$ is passed through the liquid ketone[72].
2. Schiff base + $ClNH_2$.[73] The reaction is carried out in an organic solvent. In this case *N*-chloroalkylamines react just as effectively as chloramine, which may be used to synthesise *NN′*-dialkylated diaziridines.
3. Ketone + NH_3 + HSA.[74]
4. Ketone + imine + HSA.[75]
5. *N*-Chloramino-derivative of ketone + NH_3 or amine[76].

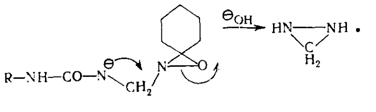
This method may be simplified when the *N*-chlorimino-derivative of the ketone (XVI) can be obtained during the synthesis by eliminating HCl from *NN*-dichloramine (XV):[77]


(39)

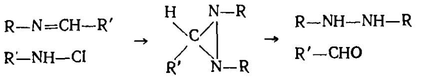
6. Oxime-*O*-sulphonic acid ($R_2C{=}N{-}OSO_3H$) + amine[78].
7. Schiff base + 3,3-dialkylaziridine[79].
8. Alkaline solutions of formaldehyde and a primary amine, in which the presence of methylenediamines may be postulated, react with hypochlorite to form diaziridines[80]:


(40)

9. The diaziridine skeleton is formed in a reaction in which it is possible to isolate a geminal intermediate stage corresponding to the intermediate stage postulated in Eqns. (36)–(38) and (40):[81]

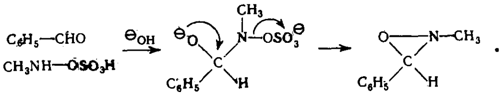

(41)

The particular importance of the synthesis of diaziridines consists in the fact that their formation is a stage in the economical syntheses of mono- and di-substituted hydrazines, which are readily formed on acid hydrolysis of diaziridines. For example, *NN*-dialkylhydrazines, which cannot be obtained by direct interaction of an amine and an *N*-chloroalkylamine, can be easily synthesised via a diaziridine by the reaction of primary amines (in the form of Schiff bases) and an *N*-chloroalkyl amine[82]:


(42)

Syntheses of Oxaziridines

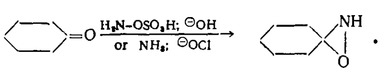
In certain cases the two-component reaction of a carbonyl compound and an aminating agent leads to the formation of the oxaziridine ring[83]:


(43)

In this case it is also possible to postulate the formation at an intermediate stage of a product resulting from addition to the carbonyl group; this is indicated, for example, by the observation that in a series of cyclic ketones the maximum yield corresponds to the six-membered ketone. Ring closure is again represented as electrophilic amination. As was to be expected for electrophilic amination, ring closure has to be catalysed by a strong base, since oxygen becomes sufficiently nucleophilic only after deprotonation.

Such syntheses of oxaziridines have been achieved using simple aliphatic ketones, cyclohexanone, and certain aromatic aldehydes. *N*-Chloromethylamine or methylhydroxylamine-*O*-sulphonic acid are usually employed as aminating agents. For higher alkyl substituents, the yields are sharply reduced.

Treatment of suitable aldehydes or ketones in an alkaline medium by aminating agents without alkyl groups leads to oxaziridines unsubstituted at the oxygen atom. The reaction has been thoroughly investigated for cyclohexanone, which gives rise to 3,3-pentamethyleneoxaziridine in 50% yield on treatment with HSA in dilute NaOH solution[79]:

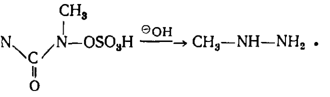

(44)

The synthesis of 3,3-pentamethyleneoxaziridine can be achieved even more simply by treating cyclohexanone with NH_3 and sodium hypochlorite[84]. The yield is about 70%. Both reactions are extremely fast. The interaction of cyclohexanone with NH_3 and hypochlorite takes place at 0° in 30 s and is at least 1000 times faster than the alkaline decomposition of chloramine in the absence of ketone. Thus the latter is involved in the rate-limiting stage of the process. One can also assume the addition of chloramine (or HSA) to the carbonyl group, which is followed by intramolecular electrophilic amination.

Diaziridinones, Iminodiaziridines, and Thiadiaziridine 1,1-Dioxides

The formation of hydrazine on treatment of urea with hypochlorite has been known for a long time[85]. To account for the course of the reaction, it is insufficient to employ the analogy with the Hofmann degradation of amides, since Ohme and Preuschhof were able to show that, although the reaction of asymmetric dimethylurea with hypochlorite yields *NN*-dimethylhydrazine [Eqn. (45)], *N*-hydroxy-*N*-methylurea-*O*-sulphonic acid (XVII) acted upon by alkali also reacts with formation of the N–N bond and gives rise to methylhydrazine [Eqn. (46)][86,87]:

$$(CH_3)_2N{-}CO{-}NH_2 \xrightarrow{\ominus OCl} (CH_3)_2N{-}NH_2\ , \qquad (45)$$

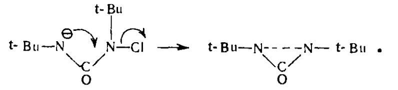

(46)

$$H_2N{-}\underset{\underset{O}{\|}}{C}{-}\overset{CH_3}{\overset{|}{N}}{-}OSO_3H \xrightarrow{\ominus OH} CH_3{-}NH{-}NH_2\ . \qquad (46)$$

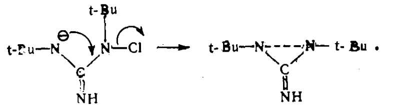
(XVII)

The first compound may be deprotonated by *N*-chlorination at the nitrogen atom, which is already linked to chlorine, creating thereby the structural precondition for the Hofmann amide degradation. In compound (XVII) only the unsubstituted nitrogen is deprotonated, which makes it more likely that the N–N bond is formed by intramolecular closure to give an intermediate three-membered ring.

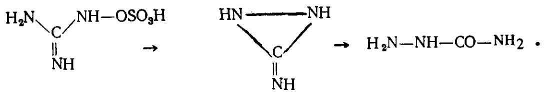
Indeed, in the presence of t-alkyl substituents at both nitrogen atoms of urea, stable diaziridinones were obtained[88]:


(47)

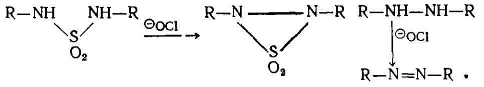
Later it was possible to obtain similarly iminodiaziridines. *N*-Chlorination of t-alkylguanidines and base-catalysed ring closure result in the formation of a three-membered ring[89]:


(48)

Before this, experiments with ^{15}N showed that semicarbazide is formed from hydroxyguanidine-*O*-sulphonic acid via an intermediate symmetrical stage, for which the structure of an iminodiaziridine was postulated[90]:

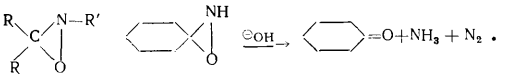

(49)

The formation of dialkylhydrazines and isoalkanes from dialkylsulphonamides by reaction with hypochlorite also proceeds via a three-membered cyclic stage, which has been recently demonstrated by the isolation of stable thiadiaziridine 1,1-dioxide[92]:

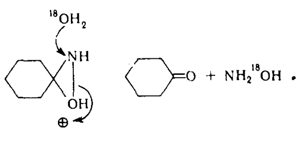

(50)

V. AMINATION BY OXAZIRIDINES UNSUBSTITUTED AT THE NITROGEN ATOM

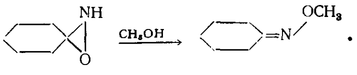
While *N*-alkyloxaziridines (XVIII) are incapable of transferring their nitrogen to other molecules, such ability is shown to a marked extent by oxaziridines (XIX) unsubstituted at the nitrogen atom, which are comparable as regards effectiveness to aminating agents known for a long time, such as chloramine and HSA. All three types of compounds are decomposed by sodium hydroxide in the same way—with formation of NH_3 and N_2:


(XVIII) (XIX) (51)

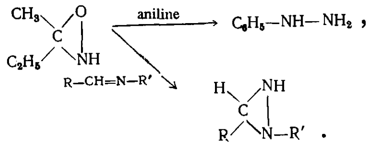
Although cleavaged by aqueous acid solution, which in the case of *N*-alkyloxaziridines is of the same type as the cleavage of acetals and leads to the formation of a carbonyl compound and an alkylhydroxylamine, has the same preparative result for compound (XIX) (the formation of a ketone and hydroxylamine), the reaction proceeds via an amination mechanism: acid hydrolysis of compound (XIX) in the presence of $H_2^{18}O$ yields hydroxylamine containing the ^{18}O isotope (52.6%). Thus amination of water competes with cleavage via the acetal mechanism[93]:


(52)

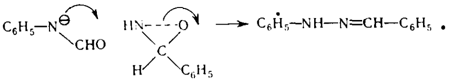
The occurrence of electrophilic amination when suitable nucleophilic agents are employed has been confirmed by the reaction products. Methanol is aminated by 3,3-pentamethyleneoxaziridine (XX) with formation of the O–N bond when the reaction is catalysed by both methoxide and strong acids[94]:


(XX) (53)

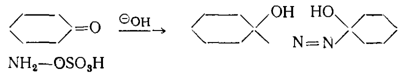
Aniline gives rise to phenylhydrazine [Eqn(54)], albeit in a yield of only 20%.[79] Aliphatic Schiff bases are aminated to diaziridines in satisfactory yields [Eqn.(55)]:[79]


(54)
(55)

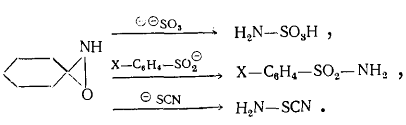
Acid amides are aminated only in the presence of strong bases as catalysts (this has been observed also for other aminating agents); after deprotonation, the amide nitrogen becomes sufficiently nucleophilic. Thus treatment of formanilide with 3-phenyloxaziridine results in the formation of benzaldehyde phenylhydrazone [reaction (56)][94]. It is remarkable that, when 3-phenyloxaziridine is decomposed by ethoxide in the absence of formanilide, a small amount of benzaldehyde phenylhydrazone is also formed. Evidently, 3-phenyloxaziridine rearranges to formanilide under the influence of the base (the two compounds are isomeric), this being following by amination in accordance with Eqn.(56):


(56)

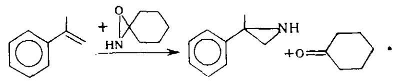
The intermediate formation of 3,3-pentamethylene-oxaziridine as the aminating agent can also be postulated in the synthesis of 1,1-dihydroxyazocyclohexane from cyclohexanone and HSA:[94]


(57)

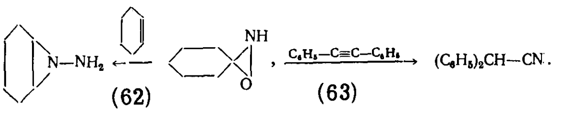
As was to be expected, strongly nucleophilic sulphur compounds are readily aminated by 3,3-pentamethylene-oxaziridine. For example, the reduction with sodium sulphite solution proceeds as amination of sulphur: sulphamic acid was isolated from the reaction mixture [Eqn.(58)][93]. The reaction with sulphinate anions also proceeds smoothly. Neutralised solutions of toluene-*p*-sulphinic acid or of *p*-chlorobenzenesulphinic acid react fully at room temperature in the course of several minutes. Sulphonamides have been isolated in 85% yield [Eqn.(59)][93]. Thiocyanate is also aminated at room temperature [Eqn.(60)][95].


(58)
(59)
(60)

It has been recently observed that 3,3-pentamethylene-oxaziridine can transfer its NH groups to olefins. For example, *p*-chlorostyrene and 1-methyl-1-phenylethylene have been converted in the course of several hours at 110°C into the corresponding aziridines in accordance with Eqn.(61), the respective yields being 58% and 46%.[96] This reaction, which has been called "enamination", is the nitrogen analogue of epoxidation. The reaction mechanism has not as yet been elucidated, but the occurrence of active intermediate stages is unlikely:


(61)

On treatment with 3,3-pentamethyleneoxaziridine, cyclohexene becomes doubly aminated; *N*-aminoaziridine was isolated as the reaction product [Eqn. (62)]:



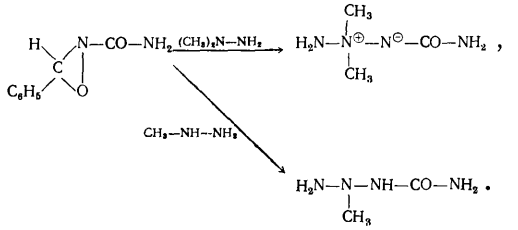
(62) (63)

Diphenylacetylene also reacts formally with addition of the NH group; after rearrangement of the phenyl groups, the reaction product is diphenylacetonitrile [reaction (63)].

VI. THE TRANSFER OF ACYLAMINO-GROUPS WITH THE AID OF *N*-ACYLOXAZIRIDINES

It has already been stated that oxaziridines alkylated at the nitrogen atom do not exhibit the aminating activity characteristic of the compounds in which the nitrogen atom is unsubstituted. On the other hand, *N*-acyloxaziridines are powerful aminating agents. Under suprisingly mild conditions, they frequently transfer the R–CON group to a nucleophilic agent.

For example, the strongly nucleophilic aliphatic hydrazines react fully even at room temperature in the course of several minutes. Triazaniumbetaine is formed in 80% yield from 2-carbamoyl-3-phenyloxaziridine and *NN*-dimethylhydrazine [Eqn. (64)][97]. Under the same conditions, methylhydrazine gives rise to triazanecarbonamide [Eqn. (65)]:



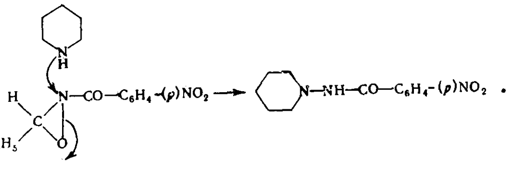
(64)

(65)

The corresponding compounds have been obtained from adducts of phenyl isocyanate or *p*-nitrophenyl isocyanate and 3-phenyloxaziridine by reaction with dialkyl- and monoalkyl-hydrazines.

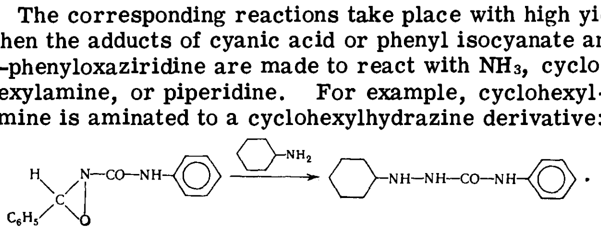
However, a precondition for the reaction is the presence of a phenyl group at the carbon atom of oxaziridine. The triazine derivatives obtained are very unstable: at room temperature they exist for several minutes. They can be obtained only by virtue of the extremely high reactivity of *N*-acyloxaziridines. The formation of the N–N bond must be again regarded as electrophilic amination. The oxaziridine is not cleaved to benzaldehyde and acylnitrene, since in the absence of a nucleophilic agent acyloxaziridines are completely stable under the reaction conditions.

Aliphatic amines react similarly to hydrazines[98]. As a result of the closure of the N–N bond, acid hydrazides or semicarbazides are formed. For example, an acid hydrazide is formed from 2-(*p*-nitrobenzoyl)-3-phenyloxaziridine and piperidine at 0°C in 92% yield in the course of several minutes:



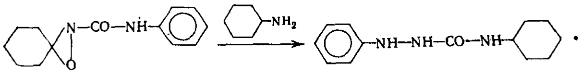
(66)

The corresponding reactions take place with high yields when the adducts of cyanic acid or phenyl isocyanate and 3-phenyloxaziridine are made to react with NH_3, cyclohexylamine, or piperidine. For example, cyclohexylamine is aminated to a cyclohexylhydrazine derivative:


(67)

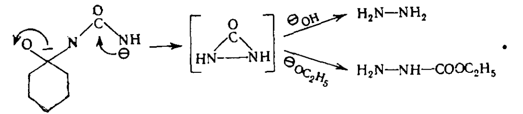
A precondition for these amination reactions is the presence of a phenyl group at the carbon atom of the oxaziridine ring.

A fundamentally different result is obtained when the oxaziridine derived from cyclohexanone is made to react with cyclohexylamine[99]:


(68)

It is very remarkable that the interaction of analogous compounds with the same reagent in accordance with Eqns. (67) and (68) yields isomeric semicarbazides, where the two substituents change places. Evidently, yet another N–N bond, joining the two nitrogen atoms of the acyloxaziridine, is formed.

This second reaction is catalysed by bases. After deprotonation, the amide nitrogen probably attacks the nitrogen in the three-membered ring [Eqn. (69)]. A new three-membered ring (diaziridinone) is then formed from the oxaziridine ring. The formation of hydrazine [Eqn. (69)] in the presence of sodium hydroxide and the formation of hydrazinecarboxylate ester in the presence of sodium ethoxide are extremely likely and have indeed been observed when the above compounds were used.



(69)

The interaction of the intermediate diaziridinone [according to Eqn. (68)] following the addition of cyclohexylamine would have led to the formation of phenylcyclohexylsemicarbazide, whose substituents would have been in the positions observed for the final product.

---o0o---

Comparison of electrophilic amination, which can also be regarded as nucleophilic substitution at a nitrogen atom, with reactions involving nucleophilic substitution at a carbon atom, shows that the latter reactions have been investigated in very great detail, including their mechanisms, while the mechanisms of nucleophilic substitution at a nitrogen atom have been very little studied.

The kinetics of the reactions of chloramine and certain alkylchloramines in the Raschig synthesis of hydrazine have been investigated. The studies of the reactions involving hydroxylamine-*O*-sulphonic acid have been concerned with syntheses on a preparative scale. The available information about amination with the aid of oxaziridines is based largely on synthetic studies and a few superficial kinetic investigations. Despite this, in the present review an attempt has been made to survey the available information from a single standpoint concerning the mechanism of electrophilic amination. This is justified to some extent by the fact that the majority of the studies discussed have been carried out in recent years and have been stimulated by definite ideas about the mechanism of the process.

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The Reactivity of Epithio-compounds†

A.V.Fokin and A.F.Kolomiets

The available information about the reactions of epithio-compounds with nucleophilic and electrophilic agents, about the homolytic reactions of alkene sulphides, and about reactions leading to the elimination of sulphur with formation of alkenes is examined, the mechanisms of the opening of thiiran rings are discussed, and the comparative characteristics of the reactivities of O- and S-heteroanalogues of cyclopropane compounds are given.
The bibliography includes 276 references.

CONTENTS

I. INTRODUCTION

The increasing interest in the chemistry of sulphur-containing organic compounds is not fortuitous and is due primarily to the urgent necessity for the utilisation of large amounts of sulphur and its simple compounds, the reserves of which are continuously increasing as a result of the increasing output of the metal extracting industry. In terms of this aspect, the chemistry of thiirans has unlimited possibilities. It is sufficient to mention that the methods of synthesising epithio-compounds developed in recent years are based on the use of sulphur chlorides, carbon disulphide, carbon oxide sulphide, metal sulphides, and other simple sulphur compounds [1].

In contrast to oxirans, the chemistry of which is closely related to the large-scale manufacture of a wide variety of substances and materials, thiirans have not as yet found extensive applications. The prospects for the practical utilisation of epithio-compounds became apparent only in the last decade. The polymerisation reactions of thiirans, which have become an independent field of study, are specially important from this point of view [2-4].

The most notable advances in the synthesis of high-molecular-weight compounds (HMC) based on thiirans have been achieved after the discovery of the high initiating capacity in these processes of organic and inorganic derivatives of zinc-subgroup metals. Using catalysts of this type, methods have been developed for the stereospecific polymerisation of racemic thiirans [5-8] and procedures for the formation of elastomeric homo- and co-polymers [9-19], thermoplastic fibre-forming high-molecular-weight compounds [20], and latexes resembling rubber latexes [21]. Polymers synthesised by this method are frequently vulcanised by sulphur [22] and can be readily worked by casting or pressing [23,24]; the articles obtained are resistant to corrosive media, solvents, and light, and possess useful mechanical properties. Elastomeric poly(alkylene sulphides) are satisfactorily covulcanised with rubbers [25,26]. The covulcanisates obtained exhibit low swellability in organic solvents and an enhanced resistance to the action of light.

Various methods for anionic and cationic polymerisation of thiirans [27-31] and for their copolymerisation with other monomers [32-35], whereby it is possible to obtain high-molecular-compounds with properties valuable in practice, have been extensively studied. The possibility of imparting water-repellent properties and of increasing the light resistance of materials made of synthetic and natural polymers by grafting poly(alkylene sulphides) on to them has also been demonstrated. The above, by no means complete, list of applications of the polymerisation capacity of thiirans shows that their practical utilisation in the immediate future is feasible.

The possibility of direct applications of thiirans has been studied much less. Among the compounds examined, there are substances with a high nematocidal activity [36] and with insecticidal [37], bactericidal [38-40], and herbicidal [41] properties. However, their use in practice is limited because of their extremely unpleasant smell. For the same reason, the use of epithio-compounds as components of pesticidal preparations is unlikely, despite their high stabilising activity [42]. The unpleasant smell makes it possible to use certain thiirans to impart an odour to gases and poisonous liquids [43].

The employment of epithio-compounds as intermediates in the synthesis of anticorrosion and antiwear additives to lubricating oils and greases, surfactants, flotation reagents, extractants, sorbents for hydrometallurgy, and pesticidal preparations is more promising. The advances achieved in research in the above fields are in many respects determined by the level of knowledge of the reactivities of the compounds.

The chemistry of epithio-compounds is at present being established. During the last ten years, studies have been made on the reactions of thiirans with a wide variety of electrophilic and nucleophilic compounds. The first qualitative and semiquantitative determinations have been made of the reactivities of thiirans. The extensive application of physicochemical methods to demonstrate the structures of the reaction products made it possible to reassess the characteristics of the reactions involving the opening of thiiran rings. For these reasons, the latest reviews on the chemistry of thiirans available to the Soviet reader [44,45] no longer reflect the present state of the problem. In the present paper an attempt is made to give a systematic account and a critical assessment of the available information about the reactivities of epithioalkanes.

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† Sulphur-containing heteroanalogues of cyclopropane derivatives are also called epithioalkanes, alkylene sulphides, and thiirans [1].

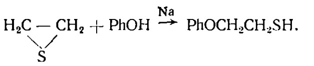
II. NUCLEOPHILIC CLEAVAGE REACTIONS

Alcohols, phenols, phosphites, thiols, organometallic compounds, primary and secondary amines, certain C–H acids, and metal hydrides have been involved in the nucleophilic opening of the three-membered ring of epithio-compounds. The characteristics of the above reactions have been by no means completely elucidated and in analysing the results one can only speak of the most general relations between the properties of the starting materials, the nature of the products, and the conditions governing their formation.

a. Reactions with Hydroxy-Compounds

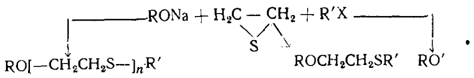
The attempts to introduce water and ethanol into reactions with 2-methylthiiran in the absence of catalysts led to the formation of a complex mixture of oligomeric products[46]. Ring opening occurred only under severe conditions (100°C). Thiiran and 2-methylthiiran react vigorously with water and alcohols in the presence of various alkaline agents[47–54], forming polymeric products. Thiiran itself polymerises particularly readily under these conditions (at room temperature). The polymerisation of 2-methylthiiran in alcoholic solutions of bases requires moderate heating. Monomeric products are not formed in reactions of thiirans with alcohols in the presence of bases and with alkali metal alkoxides.

Sodium phenoxide is said[55–57] to condense with thiiran to form 2-phenoxyethanethiol:

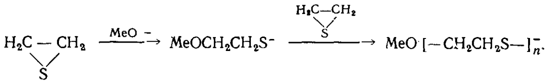


However, it has been shown recently[58] that polymerisation reactions are the main processes in this case too and monomeric products are formed in extremely small amounts.

Certain hypotheses concerning the nature of the nucleophilic reactions involving the opening of thiiran rings by hydroxy-compounds may be based on data obtained in studies of competing reactions in sodium alkoxide (phenoxide)–thiiran–electrophilic agent systems[59]. The opening of the thiiran ring by sodium methoxide and phenoxide in non-polar media proceeds at a satisfactory rate only at 40–50°C and is accompanied by polymerisation reactions. In the presence of electrophilic reagents, polymerisation reactions are suppressed. Depending on the properties of the electrophilic agent, low-molecular-weight oligomeric substances or products of the alkylation of 2-methoxy-(phenoxy)ethanethiol are formed under these conditions:

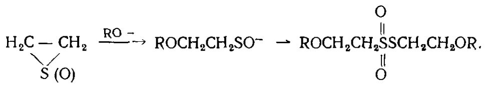


In the presence of strong electrophilic agents such as allylic alkyl halides, the reactions in the above system lead to monomeric products, and diethers of ethylene monothioglycol are formed in yields up to 50%. These results led to the hypothesis that, in media of low polarity, the electrophilic properties of thiiran and allylic alkyl halides are comparable. A study[59] has shown that the polymerisation reactions of thiirans with hydroxy-compounds in the presence of alkaline catalysts are due to the formation of thiolate anions, which are more reactive than alkoxide anions:

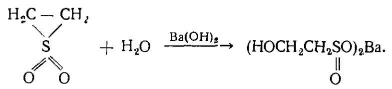


The ability of hydroxy-compounds to cleave thiiran rings comparatively readily has been used to graft poly(ethylene sulphide) and poly(propylene sulphide) to cotton, cellulose, paper, and similar materials in order to make them light resistant, water repellent, etc.[60–66].

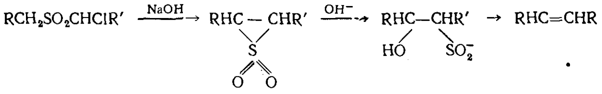
In contrast to thiirans, episulphoxides and episulphones are cleaved by hydroxy-compounds to monomeric products. On heating with water and alcohols, thiiran 1-oxide interacts according to the equation[67]



In the presence of barium hydroxide, the thiiran 1,1-dioxide ring undergoes hydrolytic cleavage under mild conditions[68]:

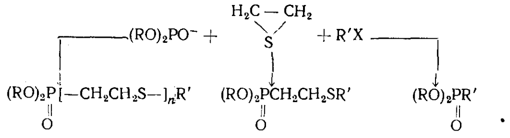


In the presence of sodium and potassium hydroxides a wide variety of alkylene episulphones, which are intermediates in the Ramberg–Baeckland rearrangement[1], react similarly:



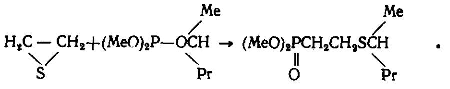
b. Reactions with Phosphites

The acidity of dialkyl phosphites is higher almost by two orders of magnitude than that of alcohols. Despite this, the reactions of sodium dialkyl phosphites with thiiran lead to polymeric products only[69]. Polymerisation takes place also when a mixture of dialkyl phosphite and thiiran is treated with sodium alkoxides. In the presence of alkyl halides, the polymerisation reactions are suppressed. In a system of competing reactions between dialkyl phosphites, thiiran, and alkyl halides, the direction of the process is determined by the relative reactivities of the electrophilic agents:



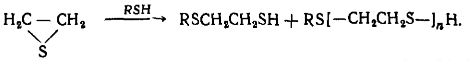
In the presence of allylic alkyl halides, the reactions proceed only with formation of monomeric products. Thus, as in the reactions with hydroxy-compounds, the polymerisation of thiiran on interaction with dialkyl phosphites in the presence of bases is a consequence of the more pronounced nucleophilic properties of the resulting thiolate anions compared with dialkyl phosphite anions:

Trialkyl phosphites eliminate sulphur from epithio-compounds under comparatively mild conditions (see below). However, according to patent data[70], phosphites with secondary alkyl groups are involved in thiiran ring opening reactions:



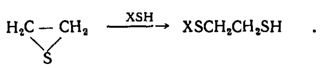
c. 2-Mercaptoalkylation of Thiols

The cleavage of the thiiran ring by thiols takes place even in the absence of catalysts. The reaction conditions are determined by the nature of the nucleophile and of the epithio-compound. According to a patent[71], aliphatic thiols interact with thiiran at 100–200°C, forming mixtures of 2-alkylthioethanethiols (up to 50%) with products of oligomerisation reactions:



2,3-Tetramethylenethiiran does not react with aliphatic thiols under these conditions[46]. According to a later report[72], thiiran condenses with thiols in the presence of a two-fold excess of the latter even at 50–70°C.

2-Mercaptoalkylation is facilitated with increase of the acidity of the thiol. Hydrogen sulphide in methanol condenses with thiiran at 45–60°C, forming ethylene dithioglycol and oligomeric products[73]. Thiophenol[72], dialkyl phosphorodithioic, phosphonothioic, and phosphonodithioic acids react under similar conditions with formation of monomeric reaction products[74–77]:

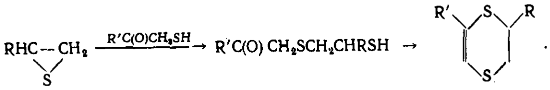


[X=Ph, (RO)$_2$P(S), R (R'C;P(S)].

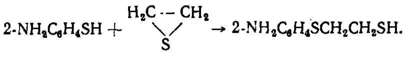
Thus unambiguous non-catalysed reactions occur only between thiirans and highly nucleophilic thiols. The relatively mild conditions of the above reactions make it possible to graft thiiran to wool fibres and human and animal hair[78,79]. In the latter case the reactions involve cysteinyl residues of protein molecules.

The condensation of thiirans with thiols is promoted by bases. 2-Methyl-, 2,3-tetramethylene-, and 2-hexylthiirans react with sodium and potassium hydrogen sulphides under mild conditions[46,80,81]. Like 2-chloromethyloxiran, 2-chloromethylthiiran forms polymeric products in this reaction[82]. The epithio-compound proved to be less reactive than its oxygen analogue. On moderate heating in the presence of sodium methoxide or ethoxide, aliphatic thiols condense with thiiran, 2,2-dimethylthiiran, and 2,3-tetramethylenethiiran[46,73,83–86]. The yield of monomercaptoalkylation products for stoichiometric proportions of the reactants does not exceed 40–50%, but may be raised to 75% by using a twofold excess of the thiol[83]. Similar results were obtained also in reactions of 2-methylthiiran[86,87], 2-mercaptomethylthiiran, and its acetyl analogue[87]. The amount of catalyst does not have a marked influence on the yield of reaction products.

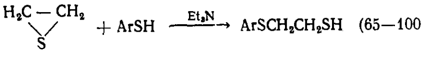
In the presence of alkali metal alkoxides, primary, secondary, and tertiary aliphatic thiols were made to react with thiirans. The yield of condensation products was found to decrease with increasing steric effects at the mercapto-group[46]. 2-Alkoxyalkanethiols react with thiirans just as readily as other primary thiols[83,85]. On reaction with thiirans, α-mercaptoketones form 2-mercaptoalkylation products, which cyclise under the reaction conditions to 2,3-dehydro-1,4-dithiane derivatives[88]:



Reactions involving 2-mercaptoalkylation of thiols catalysed by organic bases have been investigated. *o*-Aminothiophenol reacts smoothly with thiiran at 20°C [89]:

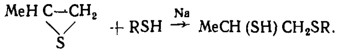


In the presence of triethylamine, thiophenol and its halogeno-, methyl-, and methoxy-substituted homologues condense with thiiran at 40–50°C [90]:

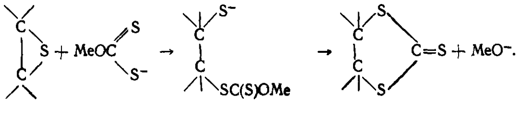


For equimolar proportions of the reactants, monomeric products are formed quantitatively when sterically unhindered thiophenols are used[91]. Quantitative 2-mercaptoethylation of aliphatic thiols and *o*-substituted thiophenols proceeds only in the presence of an excess (100–200%) of the initial thiol. The condensation of thiiran with thioacetic acid under these conditions is accompanied by polymerisation reactions.

The addition of thiophenols to thiiran in non-polar media catalysed by triethylamine proceeds with somewhat greater difficulty than the addition to oxiran[91]. Thiophenol and *p*-thiocresol are quantitatively titrated by oxiran at 20°C, while titration by thiiran requires heating above 40°C. The mode of opening of the thiiran ring by thiolate anions has been investigated[84,87,92] and it has been shown that 2,2-dimethylthiiran is cleaved mainly in accordance with Krasuskii's rule at the carbon atom with the largest number of hydrogen atoms[84]. However, products with the "anomalous" structure (primary thiols) are formed in small amounts (up to 4%). 2-Methylthiiran also reacts with thiols in accordance with Krasuskii's rule[87]. This conclusion was confirmed in a later study[92] where the structure of the condensation product was demonstrated by gas-liquid chromatography (GLC) and NMR:



Unusual reactions between thiiran and salts of thio- and dithio-carbonic acids have been discovered. Potassium methyl xanthate converts 2,3-tetramethylenethiiran into 1,2-cyclohexylene trithiocarbonate[80,93]. The reaction proceeds via a ring-opening stage according to the mechanism



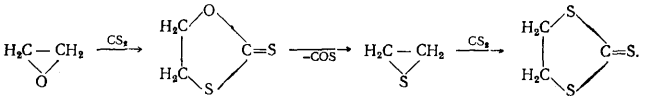
In polar media the cleavage of thiiran and oxiran rings by xanthates proceeds with equal ease. For this reason, the reactions of oxirans and thiirans with carbon disulphide and alkalis in methanol give rise to the same products—trithiocarbonates[80,93–97]. With increase of the size of the alkyl group in the xanthate, the yield of the condensation product falls because of side reactions. The reaction of ethyl xanthate with steroid epoxides already gives rise to small amounts of unsaturated compounds together with dithiocarbonates, while in the reaction with butyl xanthate the unsaturated compounds are the only products[97].

The formation of alkenes is probably associated with steric effects in the opening of the thiiran ring. In the reaction with methyl xanthate even thioglycidic acids, which readily eliminate sulphur, are smoothly converted into trithiocarbonates[98].

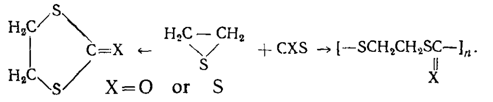
The formation of trithiocarbonates is not the only pathway in the reactions of thiirans with xanthates. High-molecular-weight compounds containing dithiocarbonic acid groups in the polymer chain react with thiiran like the usual thiols. Thus, on treatment of viscose fibres with thiirans, the xanthate groups in the polymer matrix are not split off[99]. The nucleophilic opening of the thiirans by thiols is widely used in the synthesis of polymers. By grafting poly(alkylene sulphides) to alkaline viscose, water repellent viscose fibres are obtained[99]. Elastomeric high-molecular-weight compounds have been obtained by the copolymerisation of 2-methylthiiran with 1,3-dimercaptopropane in the presence of tertiary amines[100]. Certain thiols (sodium sulphide and hydrogen sulphide, hydrogen sulphide, and 1,2-dimercaptoethane) are effective catalysts in the polymerisation of lower epithio-compounds in polar media[101]. Hydrogen sulphide and aliphatic thiols are used as effective cocatalysts of organic and inorganic zinc-subgroup metal derivatives in the polymerisation and copolymerisation of various thiirans[102-105]. Zinc xanthates[106] and iron, cobalt, and other metal mercaptides[107] have also been used as polymerisation catalysts.

d. Condensation of Thiirans with Thiono-Compounds

The possibility of the nucleophilic condensation of thiiran with thiono-compounds was suggested for the first time by Durden et al.[108] in order to explain the formation of ethylene trithiocarbonate in the reaction of oxiran with carbon disulphide catalysed by triethylamine:



Razuvaev and coworkers confirmed this hypothesis experimentally having shown that in the presence of triethylamine as the catalyst thiiran condenses with carbon disulphide[109,110] and carbonyl sulphide[111,112], forming monomeric cycloaddition products or regular low-molecular-weight polymers:

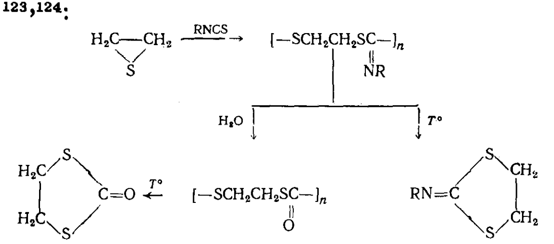


The reaction proceeds even at 20°C and at 95–100°C reaches completion in several hours. In the above reactions carbon disulphide is much more reactive than carbonyl oxide sulphide. Apart from oxiran, 3-methyloxiran and 2,3-tetramethyleneoxiran condense with carbon disulphide and carbonyl sulphide. 2-Chloromethylthiiran does not enter into these reactions probably because of the inactivation of the catalyst in the reaction mass.

The mechanism of the above reactions has not been investigated. Presumably the species initiating the process is the thiolate anion formed when the thiono-compound reacts with triethylamine. The product of its condensation with a thiiran molecule undergoes an intramolecular rearrangement or reacts with a second molecule of the thiono-compounds, propagating the polymer chain.

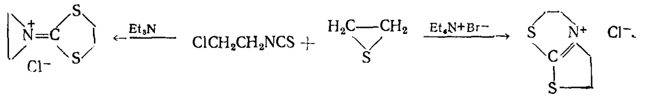
The nucleophilic addition of carbon disulphide and carbonyl sulphide to thiirans proceeds under somewhat more severe conditions than in the reactions with oxirans. As a result, the reactions of thiirans with carbonyl sulphide and carbon disulphide are used under suitable conditions to obtain epithio-compounds and alkylene monothiocarbonates and dithiocarbonates[113-122].

The thiono-compounds used in reactions with thiirans included alkyl and aryl isothiocyanates. The condensation of thiiran and 2-methylthiiran with methyl, ethyl, n-butyl, phenyl, *p*-tolyl, and α-naphthyl isothiocyanates proceeds under mild conditions in the presence of triethylamine as the catalyst. The reaction products are low-molecular-weight polymers, which are decomposed by bases and acids[123,124]:



Polymers with higher molecular weights are formed when the reactions are catalysed by butyl-lithium and sodionaphthalene[125-130]. The rate of copolymerisation of thiirans is reduced in this case with increase of the molecular weight of the isothiocyanate and when the electron-accepting properties of the substituent at the isothiocyanato-group are enhanced. The process proceeds via a stepwise mechanism with participation of "live" polymer molecules. The degree of reaction increases with increase of the basicity of the solvent, exceeding 90% in hexamethylphosphoramide. It is believed that the thiolate anion formed when the catalyst reacts with the isothiocyanate initiates the copolymerisation.

In contrast to unsubstituted alkyl isothiocyanates, 2-chloroethyl isothiocyanate reacts with thiiran to form monomeric products: 1-(1,3-dithian-2-yl)aziridinium chloride in the presence of triethylamine as the catalyst and 2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolinium chloride in the presence of tetraethylammonium bromide[131]:

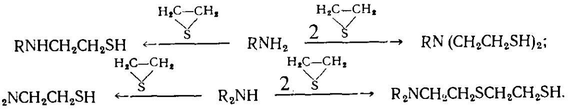


e. 2-Mercaptoalkylation of Amines

Nucleophilic reactions involving the opening of thiiran rings by nitrogen-containing compounds have been most thoroughly investigated among processes of this type. Despite this, the published studies are confined mainly to the description of the reactions of thiirans with primary and secondary amines. Ammonia, hydroxylamine, hydrazine, and acid amides and imides have not so far been 2-mercaptoalkylated.

The report of the synthesis of monomeric products of the condensation of thiirans with primary and secondary aliphatic, aromatic-aliphatic, and aromatic amines first appeared in the patent literature[132]. Thiiran and 2-methylthiiran react with amines in a closed vessel at

100–200°C. It was assumed that, depending on the reactant ratio, mono- or di-mercaptoalkylation products are formed:

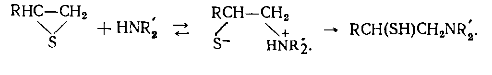


Under the conditions described in the above patent[132], thiiran was condensed with various secondary amines[133,134]. Gilmann and Woods[135] described the reaction of thiiran with lithium diethylamide and showed that the yield of product is in this case even lower than in Ref. 132. The structure of primary thiols was attributed to products of the condensation of 2-methylthiiran with amines[132], i.e. the "anomalous" opening of the thiiran ring by these substances was postulated. Hansen[136,137], who investigated the reaction of dimethylamine with thiiran and 2-methylthiiran in ether, later reached a similar conclusion.

The reactions of thiiran, 2-methylthiiran, 2,2-dimethylthiiran, and 2,3-tetramethylenethiiran with primary and secondary amines were described extensively for the first time by Snyder et al.[138], who showed that the rate of reaction of primary and secondary amines with thiirans at 100°C, using stoichiometric reactant ratios, depends significantly on steric effects. The reaction products were obtained in a high yield only from sterically unhindered amines. Amines with the iso-structure are mercaptoethylated with greater difficulty than n-alkylamines. Diphenyl- and dicyclohexyl-amines are not mercaptoethylated at 100°C. Among thiirans, the unsubstituted thiiran is the most reactive. With increase of the bulk of the substituents in the thiiran ring, the reactivity of the latter falls. Thiirans can be arranged in the following sequence in terms of decreasing capacity for cleavage by amines: thiiran > 2-methylthiiran > 2,2-dimethylthiiran > 2,3-tetramethylenethiiran.

According to Snyder et al.[138], the addition of secondary amines to 2,2-dimethylthiiran leads to the formation of tertiary mercaptans. This disproves the hypothesis of the "anomalous" opening of thiiran rings by amines and shows that the nucleophilic agent attacks the ring carbon atom with the greatest number of hydrogen atoms, in accordance with Krasuskii's rule. The "normal" cleavage of the thiiran ring by amines was subsequently demonstrated in reactions of secondary amines with 2-methylthiiran and 2,2-dimethylthiiran[139], alkoxy- and aryloxy-derivatives of 2-methylthiiran[140,141], 2-phenylthiiran[142], aminomethylthiirans[143], and 2-vinylthiiran[144].

The principal characteristics of the reactions of thiirans with amines, obtained by Snyder et al., in qualitative and semiquantitative studies, were confirmed by the kinetic data[145]. The study of the influence of the basicity of amines and steric factors on the rate of cleavage of thiiran rings in dioxan at 60°C suggested a typical S_N2 mechanism for these reactions. The first step is believed to be slow attack by the nucleophilic agent on the relatively unhindered ring carbon atom, after which there is rapid migration of a proton from the nitrogen atom to the sulphur atom:



However, Oddon and Wylde's ideas[145] concerning the formation of an intermediate dipolar adduct are doubtful. Analysis of data for the influence of the structure of the amine on the optimal conditions in the formation of monomeric condensation products suggests synchronous transfer of a proton to the sulphur atom and of the nucleophilic species to the carbon atom. Otherwise the reaction is accompanied by polymerisation processes.

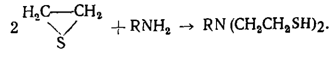
The influence of solvents on 2-mercaptoalkylation reactions of amines was discussed wisely for the first time in a report by Braz[54]. It was shown that thiiran reacts with secondary amines even without heating. In order to exclude the polymerisation of thiiran, it is desirable to carry out the reactions in an excess of the amine employed or in non-polar solvents in the presence of an excess of the amine. At 50–60°C the lower amines react rapidly with thiiran. These results[54] were confirmed by other studies and have been widely used by many investigators[146–149]. It proved possible to condense thiiran with aziridine in non-polar solvents, the two compounds copolymerising readily in the absence of a solvent[149].

Other investigators made somewhat different recommendations concerning the choice of solvents. Thus it is recommended that thiirans be condensed with highly polar amines under homogeneous conditions using their solutions in a mixture of benzene and anhydrous alcohol[148,150]. The 2-mercaptoalkylation of *N*-methylaniline by 2,3-tetramethylenethiiran proceeds smoothly in aqueous alcohol, but does not occur in the absence of a solvent[46]. 2-Phenylthiiran undergoes sulphur-elimination reactions with piperidine and morpholine in the absence of solvents[151]. Normal addition products are formed in the mixture of benzene and alcohol and the degradation of the thiiran is not observed.

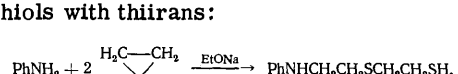
The above and other similar data[140,143,147] suggest that the optimal conditions for the 2-mercaptoalkylation reactions depend greatly on the electrophilic properties of the thiiran and on the basicity of the amine. The polarity of the medium facilitates the nucleophilic opening of the thiiran ring by amines, which may be used only in reactions with amines of low basicity. Highly basic amines can be made to react with relatively unreactive thiirans in polar solvents. The lower representatives of the class of thiirans polymerise extremely easily under these conditions. This conclusion is confirmed by the results of Reynolds and coworkers[152,153] obtained in a study of the mercaptoethylation of amines by ethylene monothiocarbonate and other similar compounds, which react via the stage involving the formation of thiiran. In the general case the formation of monomeric products of the condensation of amines with thiirans requires reaction conditions (temperature, solvent, and reactant ratio) which exclude the possibility of nucleophilic sulphur elimination and tend to reduce the stability of the sp^3-hybrid state of the nitrogen atom.

The reactions of thiirans with primary aliphatic and aromatic amines can proceed with formation of mono- and di-2-mercaptoalkylation products. Thus it has been shown[54–57,85,132,138,145–150,154–165] that, under homogeneous conditions in non-polar media and media of low polarity, substituted and unsubstituted alkylamines condense with thiirans on heating, forming mainly mono-(2-mercaptoalkyl)amines. 2-Chloromethylthiiran reacts with primary amines to form polymers[143].

Aromatic amines condense with thiirans under more severe conditions than aliphatic amines. In order to complete the reaction, heating to 100–110°C is usually necessary. The products of the condensation of an amine molecule and two thiiran molecules, which are formed to some extent in the reactions, are secondary amines according to some data[54,142]. The structure of tertiary amines was attributed to similar substances in other investigations[132,138]:



Bulavin's report[160] deals with the structure of these substances. The author showed that aniline in a non-polar solvent or in the absence of a solvent reacts with thiiran to form the tertiary amine—bis-(2-mercaptoethyl)phenylamine. The same product was obtained by condensing thiiran with *N*-(2-mercaptoethyl)aniline. Secondary amines are formed only when the reaction is catalysed by sodium ethoxide, i.e. under the conditions for the condensation of thiols with thiirans:



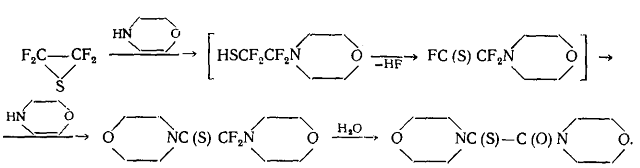
Aminoacid esters react with thiiran similarly to aniline. Thus in non-polar media thiiran can be used, like oxirans, for the exhaustive 2-mercaptoalkylation of primary amines. Under these conditions, best results are obtained in two-stage rather than single-stage synthesis[132,160].

The catalytic effects in 2-mercaptoalkylation reactions of amines have been little studied. The promoting influence of phenols in the condensation of thiiran with amines is noted in a patent[132]. However, it was later shown[138] that phenol and aluminium chloride do not catalyse these reactions.

According to patent data[166], the condensation of thiiran with primary amines is facilitated in the presence of aluminosilicates.

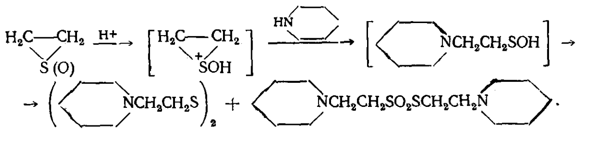
Apart from primary and secondary amines, cyanamide, guanylurea, biguanide[167–169], and monophosphorylated phenylenediamines[165] have been introduced into the reaction with thiiran. The structures of the products formed were not elucidated.

Unusual reactions occur between tetrafluorothiiran and morpholine[170]. The product of the primary cleavage of the C–S bond readily undergoes dehydrofluorination with formation of difluoro(morpholino)thioacetyl fluoride. The latter reacts with an excess of morpholine to form a morpholide, which is converted in the presence of water into the dimorpholide of thio-oxalic acid:



The reactions proceed under mild conditions, which shows that tetrafluorothiiran has marked electrophilic properties.

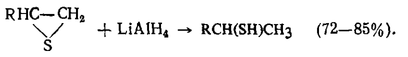
The nucleophilic opening of the thiiran 1-oxide ring by piperidine takes place readily in the presence of an acid catalyst[67]. The reaction results in the formation of di-(2-piperidinoethyl) disulphide and the 2-piperidinoethyl ester of *NN*-cyclopentamethylenethiolotaurine:



The comparatively high rates of cleavage of thiiran rings by amines are used in polymerisation processes. Ammonia, alkylenediamines, and alkylenepolyamines are effective cocatalysts of zinc-subgroup metal compounds for the preparation of polymers (copolymers) in bulk[12,21,171] and also of latexes of vulcanisable rubbers based on thiirans[21].

f. Reactions of Thiiran with Metal Hydrides and Tetrahydroborates

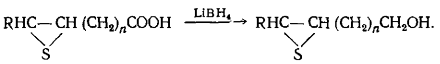
Mousseron and coworkers were the first to use lithium tetrahydroaluminate for the reduction of tetramethylthiiran and 2,3-tetramethylenethiiran[172,173]. The reaction resulted in the formation of the corresponding thiols in yields up to 85%. Later Bordwell et al.[174] used this reaction to demonstrate the mode of opening of the thiiran ring by the nucleophilic AlH_4^- species. The reduction of 2-methylthiiran, 2-butylthiiran, and 2,3-tetramethylenethiiran leads to secondary thiols, which indicates the rupture of the C–S bond involving the sterically unhindered carbon atom. The same mode of cleavage obtains in the reduction of 2-hexylthiiran[175] and 2-alkoxymethylthiirans[176] by lithium tetrahydroaluminate:



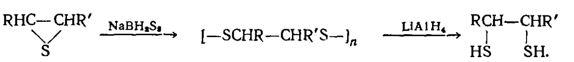
The unambiguous occurrence of the "normal" opening of the thiiran ring in reduction by lithium tetrahydroaluminate has been demonstrated by GLC[92]. The reduction process is accompanied by the inversion of the molecular configuration, as shown by data obtained in a study of the reactions of 2,3-dimethylthiiran isomers with lithium tetradeuteroaluminate[177]. Epithio-derivatives of carbohydrates are reduced similarly to the usual aliphatic epithio-derivatives[178].

A side process in the reactions discussed above is polymerisation of thiirans. In many cases this is the only process. It has been shown that, in the presence of lithium tetrahydroaluminate, 2-alkoxymethylthiirans are reduced while 2-phenoxymethylthiiran polymerises[176]. The polymerisation of 2-hexylthiiran by lithium tetrahydroaluminate proceeds readily and quantitatively in tetrahydrofuran, although in ethyl ether mainly the reduction of the thiiran takes place[175]. Polymerisation reactions in such cases are due to the pronounced polarisation of the nucleophilic agent in the reaction complex or to the specific solvation of the cation, which stabilises the thiolate anions of the final products.

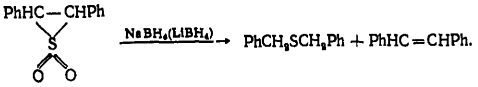
In contrast to lithium tetrahydroaluminate, tetrahydroborates do not reduce the thiiran ring under mild conditions. Thiiranylcarboxylic acids form the corresponding thiiranyl alcohols in these reactions[179]:



Sodium trithionodihydroborate behaves as a source of elemental sulphur in its reactions with thiirans[180]. The reaction results in the formation of polymers with disulphide linkages, the reduction of which yields 1,2-dimercaptoalkanes:



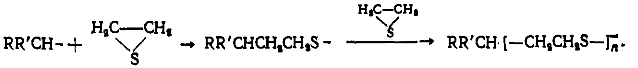
An interesting example of the reductive cleavage of the C–C bond in the thiiran ring has been described[181]. When 2,3-diphenylthiiran 1,1-dioxide reacts with sodium and lithium tetrahydroborates, dibenzyl disulphide is formed together with small amounts of a product of side reactions—stilbene:



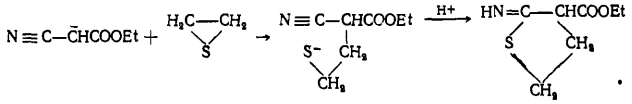
Lithium tetrahydroaluminate and sodium and lithium hydrides do not cleave the C–C bond.

g. The Opening of the Thiiran Ring by Carbanions

Despite the high basicity of carbanions, their interaction with thiirans leads to polymerisation[182]. The latter is probably due to the greater susceptibility of the thiiran ring to cleavage by thiolate anions than by carbanions:

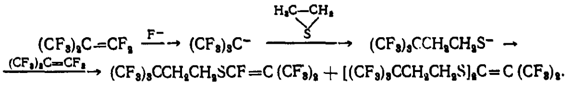


Monomeric products of the condensation of thiirans with substances generating carbanions are formed only when effective acceptors of thiolate anions are present in the reaction sphere. Examples of such reactions are the condensation of thiiran, 2-methylthiiran, and 2,2-dimethylthiiran[182] as well as 2-phenylthiiran[181] with cyanoacetic ester via the mechanism



The cyano-group of the initial compound serves as the acceptor of thiolate anion in these reactions, which leads to the formation of iminotetrahydrothiophen derivatives as cyclisation products. The above reactions are accompanied by the polymerisation of thiirans. The yield of monomeric products is higher the lower the reactivity of the thiiran competing with the cyano-group in processes involving the capture of thiolate anions.

An interesting example of the opening of thiiran rings by carbanions has been described[183]. The reaction of octafluoroisobutene with thiiran in the presence of potassium or caesium fluoride is accompanied by the nucleophilic opening of the thiiran ring and nucleophilic substitution of a fluorine atom in the perfluoro-olefin by the thiolate anion formed. The first reaction step involves the formation of the carbanion:



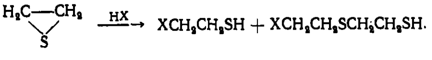
The yield of monomeric condensation products in the above reaction is higher than in the reaction of thiiran with cyanoacetic ester, which can be accounted for by the more effective capture of thiolate anions by perfluoroisobutene.

III. ELECTROPHILIC CLEAVAGE REACTIONS

A wide variety of electrophilic agents have been introduced into electrophilic reactions involving the cleavage of thiirans: hydrogen halides and their aqueous solutions, other inorganic and organic acids, halogens, carboxylic acid halides and anhydrides, sulphur, phosphorus, and arsenic halides, isothiocyanatoarsines, alkyl halides, and compounds with multiple bonds (nitriles, ketens, carbonyl and thiocarbonyl compounds, and perfluoroalkenes). Together with these, thiirans condense with nucleophilic agents (alcohols, thiols, tertiary amines) in the presence of initiators of electrophilic processes.

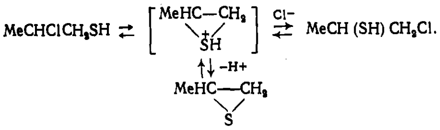
a. Reactions with Acids

Delepin and coworkers[47,49] showed that the reactions of thiiran with dilute hydrogen halides lead to the formation of polymeric products. Only in the presence of concentrated hydrochloric acid with cooling is thiiran converted into 2-chloroethanethiol[47] and in the presence of hydrobromic acid into 2-bromoethanethiol[49]. Together with monomeric substances, oligomers are formed in these reactions:

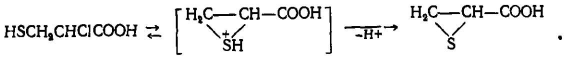


2,3-Tetramethylenethiiran and 2-chloromethylthiiran react with concentrated hydrochloric acid on cooling similarly to thiiran itself, polymerising in boiling acid[46].

The reactions of substituted alkylthiirans with aqueous hydrochloric acid solutions may be regarded as reversible. It has been shown[92] that 2-chloropropanethiol isomerises in the presence of water with formation of a mixture of substances containing about 60% of 2-methylthiiran:



α-Chloro-β-mercaptoalkanecarboxylic acids undergo similar reactions with 10% HCl.[184] In this case equilibrium is strongly displaced towards the formation of the thiiran:



The opening of the ring in these compounds also occurs only in concentrated hydrochloric acid solutions.

Anhydrous hydrogen halides in ether or methylene chloride cleave thiirans under mild conditions with formation of monomeric products only[73,92,142,185-189].

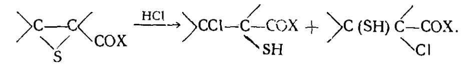
The mode of cleavage of the ring in asymmetric thiirans by hydrogen halides was investigated by chemical methods in early studies. According to some workers[185-188], the reactions of 2-methylthiiran and 2-chloromethylthiiran with hydrogen halides lead to primary thiols, i.e. the thiiran ring is cleaved "anomalously" at the ring carbon atom with the smallest number of hydrogen atoms.

Only Stewart and Cordts[190] demonstrated the occurrence of "normal" ring opening in 2-methylthiiran by hydrogen chloride. However in a later report[142] the primary thiol structure was also attributed to the product of the reaction of 2-phenylthiiran with hydrogen halides.

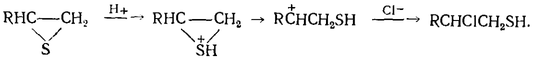
Schwarts[92] made a careful study of the mode of cleavage of the rings in 2-methyl-, 2,2-dimethyl, and 2-chloromethyl-thiirans by anhydrous hydrogen halide solutions in ether and methylene chloride by GLC and NMR. He showed that the reactions proceed in different ways, with formation of a mixture of products of the "normal" and "anomalous" ring opening. Reactions in accordance with Krasuskii's rule predominate. The content of products with the "normal" structure in the resulting mixture is 76% for 2-methylthiiran, 66% for 2,2-dimethylthiiran, and 96% for 2-chloromethylthiiran. In the presence of water or hydrochloric acid, the primary thiols formed isomerise. The content of products with the "anomalous" structure in the equilibrium mixture reaches 90–98%:

$$\underset{(76\%)}{\mathrm{MeCH(SH)CH_2Cl}} + \underset{(24\%)}{\mathrm{MeCHClCH_2SH}} \overset{H+}{\rightleftarrows} \underset{(10\%)}{\mathrm{MeCH(SH)CH_2Cl}} + \underset{(90\%)}{\mathrm{MeCHClCH_2SH}}.$$

This property of 2-halogenoalkanethiols explains to some extent the contradictory results of early investigations and of Schwarts's study of the mode of cleavage of the thiiran ring by hydrogen halides. Different types of cleavage of the thiiran ring in αβ-epithioglycidic acids and their derivatives by concentrated hydrochloric acid have been observed[184]:

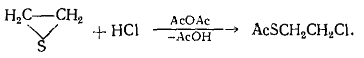


The first ideas concerning the mechanism of the reactions of thiirans with hydrogen halides were described by Davies and Savige[185,186]. The authors suggest that the reaction proceeds via the formation of an episulphonium cation, which is cleaved to the corresponding carbonium ion:



A similar reaction mechanism was proposed by Oddon and Wylde[188] on the basis of the authors' demonstration that the reactions of anhydrous hydrogen chloride and hydrogen bromide with thiiran are of second order.

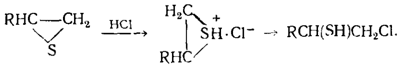
The possibility that the reactions proceed by a carbonium mechanism was confirmed in an experimental test[191]. It was shown that tetrahydrofuran, which tends to undergo reactions of this type, forms a mixture of ω-halogenobutyl acetate and 1,4-bisdiacetoxybutane in the reaction with hydrogen halides in the presence of acetic anhydride. 1,4-Bisdiacetoxybutane may be the main product when hydrogen halide is slowly introduced into a solution of tetrahydrofuran in acetic anhydride. Even under these conditions, thiiran reacts with hydrogen halides to form only 2-halogenoethyl thioloacetates:



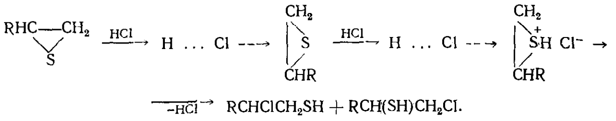
It was therefore concluded that the formation of monomeric products of the condensation of thiirans with hydrogen halides is hardly likely to be associated with the formation of carbonium ions.

Presumably only the reactions of thiirans with dilute solutions of hydrogen halides proceed via the carbonium mechanism, which is promoted by the effective solvation of the chloride ion by water molecules. In such reactions thiiran polymerises, because the carbonium ion involving the primary carbon atom is extremely electrophilic. Substituted thiirans form carbonium ions with the charge at the secondary or tertiary carbon atom. Their reduced reactivity is the reason for the stability of substituted thiirans in dilute acids noted above.

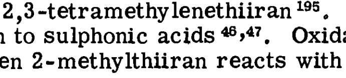
The formation of monomeric products in the reactions of thiirans with concentrated solutions or anhydrous hydrogen halides is a consequence of the formation and opening of the thiiranium halide ring in a close ion pair, which should lead to the formation of "normal" cleavage products:



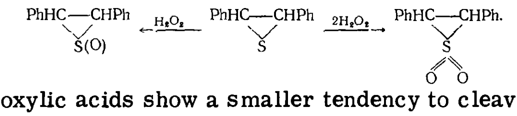
The low basicity of the sulphur atom in thiirans suggests the possibility that the reaction proceeds via a trimolecular mechanism involving the preliminary formation of π complexes:



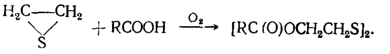
The reactions of thiirans with other inorganic acids have been little investigated. Sulphuric acid is an active initiator of the polymerisation of thiiran[47–49], 2-methylthiiran[48], 2-chloromethylthiiran[192,193], tetramethylthiiran[194], and 2,3-tetramethylenethiiran[195]. Nitric acid oxidises thiiran to sulphonic acids[46,47]. Oxidative cleavage also occurs when 2-methylthiiran reacts with hydrogen peroxide[190]:



Thiiran is converted under these conditions into poly(ethylene sulphones)[68,196] and arylthiirans react without ring opening[197,198]:



Carboxylic acids show a smaller tendency to cleave thiiran compounds. Thiiran polymerises slowly in acetic acid and 2-methylthiiran and butylene sulphide remain unchanged in acetic acid solutions in the absence of heat[47,48]. 2,3-Tetramethylenethiiran condenses with acetic acid on heating, forming a mixture of monomeric and oligomeric products[146,199]. Under severe conditions, higher carboxylic acids condense with thiiran[200]. In the presence of oxygen, the 2-mercaptoethyl ethers formed initially are oxidised to disulphides:

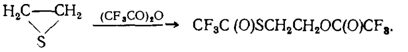


In contrast to unsubstituted carboxylic acids, trifluoroacetic acid undergoes an exothermic reaction with thiiran, initiating its polymerisation under any conditions and for any order of mixing of the reactants[201]. Thiiran reacts smoothly with perbenzoic acid, forming polymers of thiiran 1,1-dioxide[68]. Substituted thiirans are oxidised by peracids to thiiran oxides and dioxides[197,198].

b. Reactions with Carboxylic Acid Anhydrides

The anhydrides of unsubstituted carboxylic acids condense with thiiran[192,200,202,203], 2-methylthiiran[92,185], 2,2-dimethylthiiran[186], and 2,3-tetramethylenethiiran[109] under severe conditions in the presence of pyridine as the catalyst. The reaction products are diesters of 2-mercaptoalkanols. Only epithio-derivatives of steroids fail to react with acetic anhydride even in the presence of pyridine[204,205].

According to some data[185,186], the cleavage of the thiiran ring by acetic anhydride takes place in accordance with Krasuskii's rule and is a second-order process. An S_N2 reaction mechanism was therefore postulated. However, subsequently it was shown that the opening of the ring of 2-methylthiiran by acetic anhydride takes place in different ways. The proportions of the products with the "normal" and "anomalous" structures (86 and 14%) in these reactions are almost the same as in the analogous reactions with hydrogen halides. It was also shown that the reactions of acid anhydrides with thiiran are promoted not only by bases but also by their hydrochlorides and the ease of reaction is determined primarily by the reactivity of the anhydride. Trifluoroacetic anhydride undergoes an exothermic reaction with thiiran even in non-polar media without catalysts[201]:

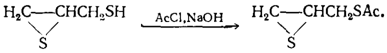


Thus the above reactions can be regarded as the usual processes involving electrophilic cleavage of thiirans.

c. Reactions with Acyl Halides

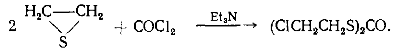
Acetyl, chloroacetyl, and aroyl chlorides as well as the bromides and iodides of aliphatic and aromatic carboxylic acids have been made to react with a wide variety of thiirans. According to Ivin's data[206], acid chlorides react only on heating. Acid bromides and particularly iodides undergo exothermic reactions with thiiran and 2-methylthiiran. With increase of the molecular weight of the acid halide, its capacity for condensation with thiirans diminishes. Aroyl chlorides react with greater difficulty than acetyl chloride[46]. 3,5-Dinitrobenzoyl chloride and benzoyl fluoride initiate the polymerisation of thiiran and their reactions with the latter compounds do not lead to monomeric products.

A wide variety of thiirans, including unsubstituted thiiran[136,203,206-208], 2-methylthiiran[46,92,185,206,209], 2-chloromethylthiiran[46,73,92,186], 2,2-dimethylthiiran[92], 2-phenylthiiran[142], and 2,3-tetramethylenethiiran[46,199] condense smoothly with acyl halides. 2-Mercaptomethylthiiran reacts smoothly with acetyl chloride in the presence of bases to form 2-acetylthiomethylthiiran[210,211]:



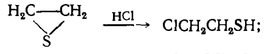
On heating, chlorocarbonic esters react with thiirans similarly to acyl chlorides[212]:

Phosgene undergoes exothermic condensation with thiiran and 2-methylthiiran via only one C–Cl bond. The attempts to achieve exhaustive substitution by 2-chloroethylthio-groups on heating were unsuccessful. Only in the presence of triethylamine as catalyst does the phosgene molecule condense with two thiiran molecules[213]:



Tertiary amines in the presence of traces of moisture or tertiary amine hydrohalides are effective catalysts of the reactions of thiiran with relatively unreactive acyl chlorides[208]. In the presence of pyridine hydrochloride or pyridine and moisture at 40–60°C thiiran condenses quantitatively with aryloxyacetyl chlorides. In the absence of catalysts, thiiran polymerises. The following mechanism may be postulated for the above reaction:

$$RC(O)Cl + Py \cdot HCl \rightarrow RC(O)Py^+Cl^- + HCl;$$



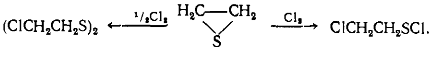
$$RC(O)Py^+Cl^- + ClCH_2CH_2SH \rightarrow RC(O)SCH_2CH_2Cl + Py \cdot HCl.$$

The opening of the 2-methylthiiran and 2-chloromethylthiiran rings by acetyl chloride and acetyl iodide and of the 2-methylthiiran ring by phosgene proceeds "anomalously" at the secondary ring carbon atom according to a number of investigations[185,206,212]. However, it has been shown by GLC and NMR [92] that mixtures of substances are formed in the reactions of 2-methyl-, 2-chloromethyl, and 2,2-dimethyl-thiirans with acetyl chloride and bromide and also with aroyl chlorides. The products of the "normal" cleavage of thiiran rings are mainly formed (54–85%). Only in the reaction of 2,2-dimethylthiiran with acetyl chloride do the "anomalous" pathways, accompanied by the formation of isobutenyl thioloacetate, predominate.

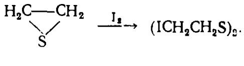
It is striking that in the 2-methylthiiran–*p*-aroyl chloride series a significant influence of the ring substituent on the proportions of the "normal" and "anomalous" products was not demonstrated[92]. The insignificant influence of the electrophilic properties of the acyl chloride on the mode of thiiran ring opening indicates a complex mechanism of the above reactions. Depending on the nature of the reactants employed and the reaction conditions, the electrophilic opening of the thiiran ring by acyl halides occurs to some extent via the carbonium mechanism or via the formation of an acyl sulphonium ion and the cleavage of the ring of the latter in the state of a contact ion pair. In many cases the process is decisively influenced by the presence of traces of moisture in the reaction sphere and by the involvement of the hydrogen halide in the ring opening step.

d. Reactions with Halogens

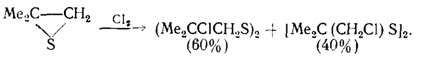
The earlier attempts to halogenate thiirans under severe conditions were unsuccessful. The exothermic reaction of thiiran with bromine yielded a viscous product of unidentified composition. 1,2-Dichlorocyclohexane and polymeric products were obtained by the chlorination of 2,3-tetramethylenethiiran under similar conditions[46,47]. The extensive study of the above reactions began only after the investigations by Stewart[192,214], who achieved the chlorination and bromination of 2-methylthiiran under mild conditions. It is now known that thiiran[215], 2-methylthiiran[92,192,214,215], 2-chloromethylthiiran[92,143], 2-phenylthiiran[142], and 2,2-dimethylthiiran[92,142] are smoothly chlorinated in solution in halogenoalkanes. In the absence of traces of moisture from the reaction, the halogenation reactions are not accompanied by the polymerisation of the thiirans and are usually completed after the introduction of the halogen into the reaction sphere. Depending on the reactant ratio, di-(2-halogenoalkyl) sulphide or 2-halogenoalkylsulphenyl halides are formed:



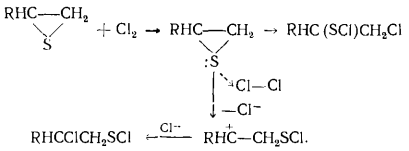
Like chlorine, sulphuryl chloride readily enters into the reaction[215]. The iodination of thiiran, 2-methylthiiran, and 2,3-dimethylthiiran is completed at the stage involving the formation of di-(2-iodoalkyl) sulphides:



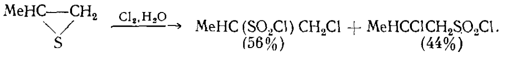
In order to demonstrate the mode of ring opening, the products of the halogenation of 2-methylthiiran were converted into derivatives of 2-substituted alkanesulphonic acids the properties of which were compared with those of substances of known structure[192,214]. The "normal" opening of the thiiran ring was demonstrated in this way. The mode of 2-methylthiiran ring opening was also established by condensing with alkenes the 2-halogenoalkanesulphenyl halides formed in the reaction and by identifying the resulting sulphides in the form of their derivatives[215]; the "anomalous" opening of the 2-methylthiiran ring was thus demonstrated. Schwarts[92] showed by GLC and NMR that the above reaction takes place in several ways. The main products in the resulting mixture have the "normal" structure (55–85%), but in 2,2-dimethylthiiran the C–S bond is cleaved preferentially at the tertiary carbon atom:



It is of interest that under the usual conditions tetrafluorothiiran does not interact with chlorine and bromine[170]. The reaction apparently requires comparatively marked nucleophilic properties of the ring heteroatom, which creates conditions favouring the heterolytic addition of a halogen molecule to the thiiran:

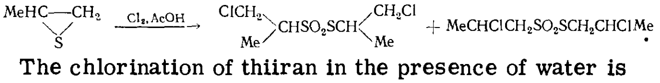


The chlorination and bromination of 2-methylthiiran in the presence of water and other hydroxy-compounds leads to the formation of products of the oxidative cleavage of the ring[92,192,214]. It has been shown[92] that the exhaustive oxidation of 2-methylthiiran by chlorine in water results in a mixture of substances where "normal" ring opening predominates:

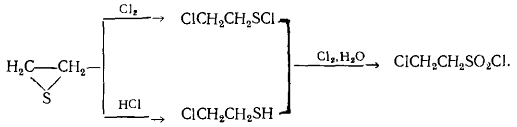


The proportions of the "normal" and "anomalous" products are the same as in chlorination under anhydrous conditions. This suggests that the oxidative processes take place after the opening of the thiiran ring, which occurs in aqueous media via the same mechanism as under anhydrous conditions.

Exhaustive oxidative ring cleavage also occurs in the chlorination of 2-phenylthiiran[142] and 2-chloromethylthiiran[143] in aqueous acetic acid. In anhydrous acetic acid it is also possible to obtain a product of the partial oxidation of 2-methylthiiran by chlorine[192]. In this case a mixture of isomeric 2-chloroalkanethiyl esters of 2-chloroalkanesulphonic acids is probably formed:

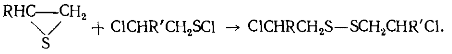


The chlorination of thiiran in the presence of water is always accompanied by the polymerisation of the former[217]. The reason for this is the unusually high capacity of thiiran for polymerisation via a cationotropic mechanism. The conditions for such reactions are created at the very beginning of the process on formation of a dilute HCl solution. The chlorination of thiiran in the presence of concentrated hydrochloric acid makes it possible to eliminate polymerisation reactions and to obtain 2-chloroethanesulphonyl chloride in a high yield. The unambiguous course of the reactions is in this case due to the involvement of hydrogen chloride in the ring opening processes:

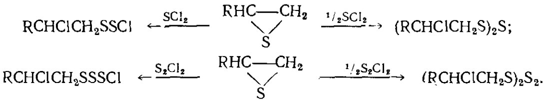


e. Reactions with Non-Metal Halides

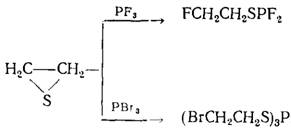
Sulphur halides react smoothly with thiirans in non-polar media[218,219]. Thus sulphenyl chlorides condense, on cooling their solutions in carbon tetrachloride, with thiiran, 2-methylthiiran, and 2,2-dimethylthiiran, forming the corresponding disulphides. According to Epshtein et al.[218], "anomalous" ring opening takes place in these reactions:



Sulphur chlorides react with thiirans under similar conditions[219]. Depending on the reactant ratio, di- and tri-sulphenyl chlorides or tri- and tetra-sulphides are formed in the reactions of sulphur monochloride and dichloride with thiiran and 2-methylthiiran. The structures corresponding to the "anomalous" ring cleavage were also attributed to these products:

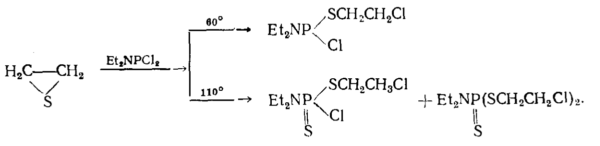


The reactions of phosphorus halides with thiiran proceed less smoothly. According to patent data[220–222], phosphorus trifluoride and tribromide condense with thiirans, forming 2-halogenoalkanethiol esters:

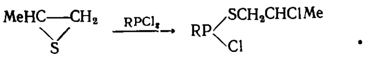


Phosphorus chloride dibromide and dichloride bromide as well as phosphoryl bromide react similarly.

Phosphorus trichloride condenses with thiiran and 2-methylthiiran only in the presence of zinc chloride. Depending on the reactant ratio, mono- and di-addition products are formed[223,224]. Exhaustive substitution by 2-chloroalkylthio-groups is accompanied by the polymerisation of thiirans. In the absence of catalysts, *NN*-diethylphosphoramidous dichloride reacts with thiirans on moderate heating (60–70°C), forming small amounts of monoaddition products. On heating above 100°C, a mixture of phosphorodithioate and phosphorotrithioate was obtained:

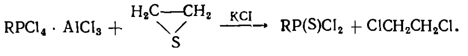


Alkyldichlorophosphines condense unambiguously with thiiran and 2-methylthiiran via one P–Cl bond[225,226]. It is assumed that the opening of the 2-methylthiiran ring takes place at the secondary carbon atom:



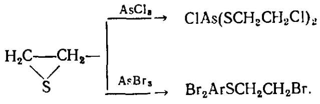
Condensation reactions between thiirans and phosphorous(III) chloride apparently takes place in steps. This may be a consequence of inductomeric and weaker mesomeric effects of the 2-chloroalkanethiol groups. The presence of substituents with a strong *+M* effect (amino-groups) at the phosphorus atom virtually rules out the possibility of condensation.

Among other phosphorus compounds, complexes of alkyltetrachlorophosphoranes and aluminium trichloride have been made to react with thiiran[227,228]. The reaction is accompanied by the elimination of sulphur from thiiran:

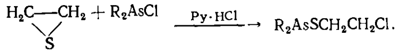


Phosphorus pentafluoride initiates the polymerisation of thiirans and does not form monomeric products on reacting with them[229,230].

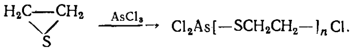
In dilute carbon tetrachloride solutions arsenic halides condense with thiiran, forming monomeric products in low yields[231]:



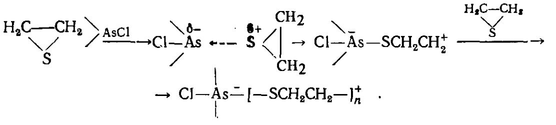
Under these conditions, arsenic trifluoride initiates the polymerisation of thiiran. Dialkylchloroarsines and alkyldichloroarsines condense with thiiran even in concentrated solutions and in the presence of pyridine or its hydrochloride as catalysts are converted quantitatively into 2-chloroethylthioarsinites[232]:



The reactions of thiiran with arsenic trichloride in concentrated solutions lead to oligomeric products even in the presence of catalysts:

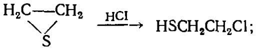


The ability of arsenic chlorides to initiate the polymerisation of thiiran increases in the series of compounds characterised by decreasing electron density at the arsenic atom ($R_2AsCl < RArAsCl < Ar_2AsCl < RAsCl_2 < ArAsCl_2$). This suggests that polymerisation reactions are caused primarily by the strength of the $3p_\pi-4d_\pi$ bonding between the sulphur and arsenic atoms in the reaction complex and by the low reactivity of the chlorine atoms in it:



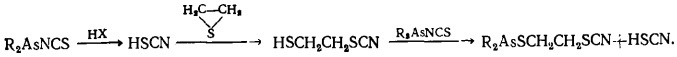
The catalytic effect of pyridine hydrochloride is due to the appearance in the reaction sphere of highly reactive hydrogen chloride and the activation of nucleophilic substitution at the arsenic atom:

$$R_2AsCl + Py \cdot HCl \rightarrow R_2AsPy^+Cl^- + HCl;$$



$$R_2AsPy^+Cl^- + HSCH_2CH_2Cl \rightarrow R_2AsSCH_2CH_2Cl + Py \cdot HCl.$$

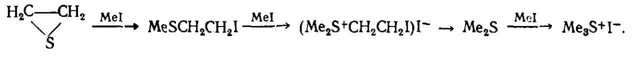
Dialkylisothiocyanatoarsines react with thiiran similarly to chloroarsines[223,234]. The reactions proceed only in the presence of substances promoting the formation of thiocyanic acid in the reaction sphere, which is the reason for the anomalous conversion of isothiocyanatoarsines into 2-thiocyanatoethyl thioarsinites:



In contrast to sulphur, phosphorus, and arsenic halides, halogenosilanes, and isothiocyanatosilanes do not interact with thiiran even in the presence of catalysts[235].

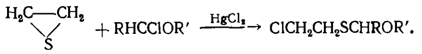
f. Reactions with Alkyl Halides

According to Merill and Perkins[194], the reaction of tetramethylthiiran with methyl iodide is more difficult than the corresponding reaction of acyclic sulphides. Regardless of the nature of the thiiran employed, the reaction leads to the formation of trimethylsulphonium iodide[46,236–238] and not *S*-alkylthiiranium iodide. The available data suggest that the primary reaction products are unstable. The opening of their rings leads to polymerisation reactions and to partial formation of linear sulphides. The latter are readily iodomethylated, which leads to degradative transformations:



2-Phenylthiiran is alkylated by dimethyl sulphate at room temperature[239]. However, in this case the thiiranium salt or its monomeric cleavage product were not isolated either. Only 2,5-diphenyldithiane was isolated in a low yield.

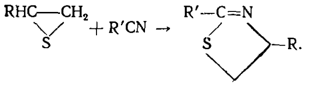
The usual products of the electrophilic opening of the rings of thiiran and 2-methylthiiran were obtained only when the latter reacted with alkyl *α*-chloroalkyl ethers in the presence of mercury(II) chloride[240]:



The reactions proceed under mild conditions. The "anomalous" cleavage of the 2-methylthiiran ring by alkyl *α*-chloroalkyl ethers is postulated.

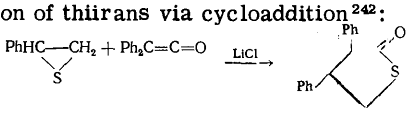
g. Cycloaddition Reactions of Thiirans

Several examples of such reactions are known. In the presence of strong inorganic acids the nitriles of aliphatic acids and thiirans react to form thiazolines[241]:



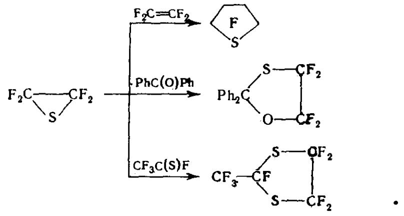
The condensation reactions are stereospecific, which shows that the cycloaddition proceeds via a stage involving the formation of a *π* complex of the thiiran molecule and the iminocarbonium ion. The thiirans polymerise simultaneously with condensation, in consequence of their cationotropic reactions.

The reaction of diphenylketen with 2-phenylthiiran in the presence of lithium chloride is the next example of the condensation of thiirans via cycloaddition[242]:

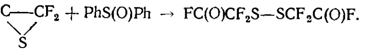


Thiiran and its aliphatic derivatives polymerise under these conditions.

A high capacity for cycloaddition reactions is characteristic of tetrafluorothiiran[170]. This compound condenses with tetrafluoroethylene to form octafluorotetrahydrothiophen, with benzophenone to form 2,2-diphenyloxathiolan, and with thioacetyl fluoride to form 1,3-dithiolan:



Only diphenyl sulphoxide enters into exchange reactions with tetrafluorothiiran:

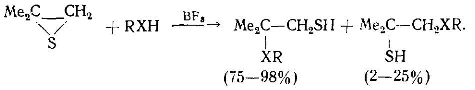


$$F_2C{-}CF_2 + PhS(O)Ph \rightarrow FC(O)CF_2S{-}SCF_2C(O)F.$$

h. Electrophilic Condensation Reactions with Nucleophilic Agents

The condensation reactions of thiirans with alcohols and thiols in the presence of boron trifluoride or boron trifluoride-ether have been investigated[142,183-185] and it has been shown that 2,2-dimethyl- and 2-phenyl-thiirans give rise to monomeric products in 20–40% yield on reaction with primary alcohols and thiols. Steric effects at the nucleophilic centre lead to a sharp decrease of the yield of monomeric products. 2-Methyl- and 2,3-tetramethylene-thiirans polymerise in these reactions.

According to conductimetric titration data, the products of the condensation of 2,2-dimethylthiiran and alcohols and thiols consist of a mixture of substances in which the "anomalous" isomers predominate:



$$\underset{S}{Me_2C{-}CH_2} + RXH \xrightarrow{BF_3} \underset{\substack{XR\\(75-98\%)}}{Me_2C}{-}CH_2SH + \underset{\substack{SH\\(2-25\%)}}{Me_2C}{-}CH_2XR.$$

Similar results were obtained also in the reaction of ethanol with 2-phenylthiiran catalysed by sulphuric acid[243].

The condensations of thiiran with lauryl alcohol and nonylphenols were investigated recently in the presence of catalysts for electrophilic reactions[58]. It was established that HCl, $SnCl_4$, and BF_3 promote the formation of 2-mercaptoethylation products. However, the yield of monomeric substances is low and polymeric products are mainly formed.

An example of the condensation of tertiary amines with 2-methylthiiran in the presence of boron trifluoride-ether and sulphur dioxide has been described[244]:

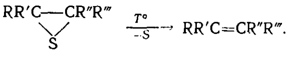
$$\underset{S}{MeHC{-}CH_2} + Me_2NR + SO_2 \xrightarrow{Et_2O\cdot BF_3} {}^{-}O_2SSCH_2CHMe{-}\overset{+}{N}Me_2R.$$

IV. ELIMINATION OF SULPHUR

The capacity to split off sulphur is one of the characteristic properties of thiiran. Sulphur is usually eliminated on pyrolysis and on moderate heating in the presence of metals, metal oxides, and bases.

a. Pyrolytic Elimination of Sulphur

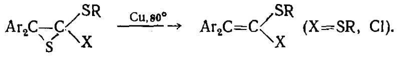
The thermal stability of thiirans depends significantly on their structure. The presence of electronegative substituents at the ring carbon atoms sharply increases the tendency of the thiiran to split off the sulphur atom. On heating, sulphur is readily eliminated from tetraarylthiirans[243-245], 2,2-diaryl-3,3-diethylthiirans[246], tetrachlorothiirans, and symmetrical diaryldichlorothiirans[247]:



$$\underset{S}{RR'C{-}CR''R'''} \xrightarrow[-S]{T^\circ} RR'C{=}CR''R'''.$$

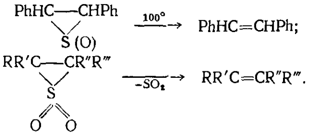
Monosubstituted thiirans, including 2-phenylthiiran[151], 2,3-tetramethylenethiiran[195], and 2-hexylthiiran[175] split off sulphur with somewhat more difficulty.

The elimination of sulphur takes place particularly readily (and quantitatively) in the presence of copper bronze[248-250]. The mild conditions in this sulphur elimination reaction make it possible to obtain even relatively unstable keten mercaptals and their derivatives[248,249]:



Zinc oxide is a less effective sulphur-eliminating agent[251].

Thiiran 1-oxides are converted into olefins on heating in toluene[252]. The 1,1-dioxides are cleaved even more readily on heating[253-256]:



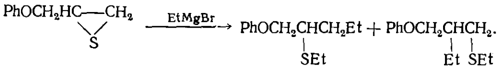
Thiirene 1,1-dioxides, which are more stable than thiiran dioxides, also tend to split off sulphur dioxide[257].

Investigations have shown that the pyrolytic elimination of sulphur from thiirans takes place via a homolytic mechanism. The deformation of the heterobonds as a result of the involvement of the ring electrons in π-conjugated systems greatly facilitates the process. The ease of the homolysis of heterobonds in the thiiran ring is attributed to the weak bonding and antibonding nature of the C–S σ bonds.

b. Elimination of Sulphur in Nucleophilic Thiiran Ring Opening Reactions

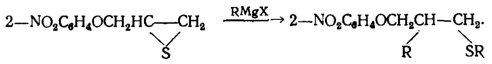
The elimination of sulphur from thiirans is promoted by bases. αβ-Epithioglycidic acids and their derivatives[93,184] and 2,3-diphenylthiiran[93] split off sulphur in the presence of bases even at room temperature. Secondary amines eliminate sulphur from 2-phenylthiiran in non-polar media[151].

When 2,3-tetramethylenethiiran and substituted 2-methylthiirans are treated with Grignard reagents and other organometallic compounds in non-polar media, sulphur is eliminated from the thiirans[174,238]. It has been shown for the reactions of *cis*- and *trans*-butene sulphides with butyllithium that this process is stereospecific[258]. In many instances Grignard reagents behave also as alkylating agents in relation to thiirans. According to Takeda[141], phenoxymethylthiiran reacts with ethylmagnesium bromide to form a mixture of "normal" and "anomalous" products:



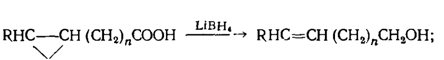
$$\underset{S}{PhOCH_2HC{-}CH_2} \xrightarrow{EtMgBr} PhOCH_2\underset{SEt}{CH}CH_2Et + PhOCH_2\underset{Et}{CH}\underset{SEt}{CH_2}.$$

Higher alkyl magnesium bromides react with phenoxymethylthiiran to form only "normal" products of thiiran ring cleavage and with *o*-nitrophenoxymethylthiiran to form only the "anomalous" products:

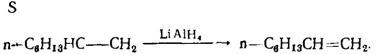


$$2\text{—}NO_2C_6H_4OCH_2HC\text{—}CH_2 \xrightarrow{RMgX} 2\text{—}NO_2C_6H_4OCH_2CH\text{—}CH_2 .$$

When thiiranylalkanecarboxylic acids are reduced by lithium tetrahydroborate[179] and 2-hexylthiiran is reduced by lithium tetrahydroaluminate[175], alkenes are also formed:



$$RHC\text{—}CH(CH_2)_nCOOH \xrightarrow{LiBH_4} RHC{=}CH(CH_2)_nCH_2OH;$$

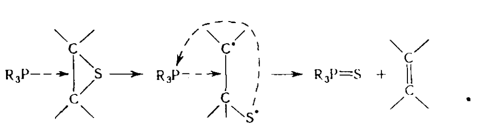


$$n\text{-}C_6H_{13}HC\text{—}CH_2 \xrightarrow{LiAlH_4} n\text{-}C_6H_{13}CH{=}CH_2 .$$

The latter reaction occurs only in non-polar media. In tetrahydrofuran 2-hexylthiiran polymerises. Sulphur is also eliminated in the reactions of epithio-derivatives of steroids with higher alkyl xanthates[97]. Conditions favouring nucleophilic sulphur elimination reactions and the similarity of the effects of structural factors on the pyrolytic and nucleophilic sulphur elimination processes indicate their homolytic mechanisms. Ring opening in nucleophilic sulphur elimination reaction proceeds most probably at the stage involving the formation of transition complexes comprising the thiiran and the nucleophilic agent under conditions preventing charge transfer.

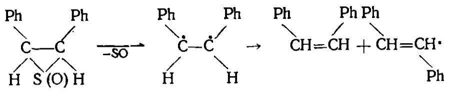
c. Elimination of Sulphur by Phosphites and Phosphines

Trialkyl phosphites and phosphines behave as nucleophilic agents in such reactions. Their inability to dissociate, low polarity and polarisability, and their high capacity for the homolytic formation of the thiophosphoryl linkage determine an unambiguous course of the process. The results obtained in a number of studies[46,176,238,258-266] show that the ease of sulphur elimination depends primarily on the basicity of the nucleophilic agent. Thus sulphur is eliminated by triethyl phosphite only on heating (100–110°C), while tributyl- or triphenyl-phosphine eliminates sulphur even at 20°C. The rate of reaction depends little on the polarity of the solvent and is of first order with respect to each reactant. The process is sterospecific to the extent of 99–100%. All these factors are consistent with a homolytic mechanism of the sulphur elimination process:

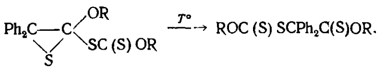


V. FREE-RADICAL REACTIONS

Free-radical reactions are to a large extent characteristic of thiirans with electronegative substituents at the ring carbon atoms. The commonest reactions of this type are the pyrolytic syntheses of alkenes from thiirans. The free-radical mechanism of the pyrolytic reactions of the thiiran ring have been demonstrated[252]. Thermal degradation of *trans*-2-phenylthiiran 1-oxide takes place stereospecifically with quantitative formation of *trans*-stilbene. Pyrolysis of the *cis*-isomer is accompanied by racemisation. This indicates the intermediate formation of a biradical, tending to isomerise with formation of the energetically more favourable conformer:

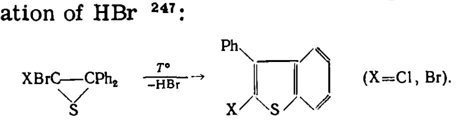


The free-radical mechanism of the pyrolytic transformations of thiirans is the cause of their unusual reactions. For example, the pyrolysis of *S*-(2-alkoxy-3,3-diaryl-2-thiiranyl) xanthates leads to mercaptoacetic acid derivatives instead of olefins[266]:



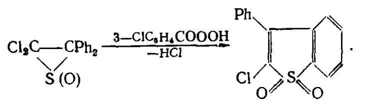
$$\xrightarrow{T^\circ} ROC(S)SCPh_2C(S)OR.$$

The pyrolysis of 2,2-diaryl-3,3-dichlorothiirans is accompanied by the formation of olefins. However, their bromo-derivatives rearrange to derivatives of benzo[*b*]thiophen with elimination of HBr[247]:

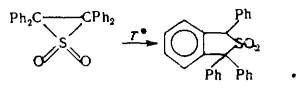


(X=Cl, Br).

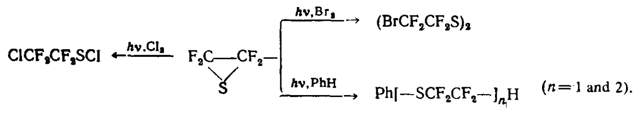
The thiiran–thiophen rearrangement takes place also in oxidative reactions of certain thiirans[202]:



In the above examples the C–S bond undergoes homolytic cleavage. An example of pyrolytic ring opening at the C–C bond is also known. Thus tetraphenylthiiran 1,1-dioxide isomerises to a dihydroisothianaphthene derivative on heating[267]:



Polyfluorothiirans undergo free-radical reactions particularly readily[170,268,269]. On irradiation with ultraviolet light, they are readily chlorinated and brominated and condense with benzene:



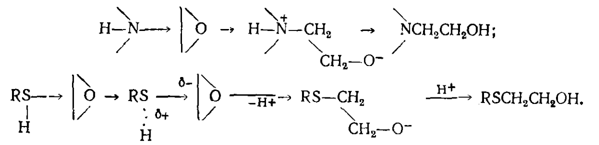
Tetrafluoro- and chlorotrifluoro-thiirans polymerise on irradiation or in the presence of di(trifluoromethyl) disulphide and form copolymers with ethylene and propene.

Thiiran and its simplest homologues show a smaller tendency to undergo free-radical reactions. On being irradiated, these substances polymerise[270,271], but the quantum yield of the reactions is comparatively low. Radical reactions are facilitated in the presence of substances capable of forming charge-transfer complexes[272]. This suggests that the increased stability of thiiran and its alkyl-substituted homologues under the conditions of homolytic reactions is a consequence of the oscillatory properties of the heterobond in their rings, associated with the low probability that the $n \rightarrow \sigma^*$ transitions of the lone electron pairs of the sulphur atoms to the antibonding orbitals of the C–S σ bond will become allowed. A similar phenomenon has been noted in a study of poly(alkylene sulphides), the free-radical reactions of which involve the dissociation of C–C bonds and not C–S bonds[273].

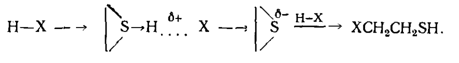
VI. CONCLUSION

The present state of the chemistry of thiirans is to a large extent determined by the development of the comparative chemistry of three-membered heterocycles. Comparison of the properties of thiirans and their oxygen analogues, the heteroatoms of which have the same number of valence electrons in different energy states, is of greatest interest.

There are no unambiguous hypotheses concerning the relation between the reactivities of oxirans and thiirans. However, it is frequently stated that the rates of cleavage of thiiran rings are somewhat lower than those of oxiran rings. Our comparison of the data presented in this review with surveys of the chemistry of liquid-phase reactions of oxirans[44,274] failed to confirm such ideas and showed that an unambiguous answer to this question, unrelated to the reaction conditions, is impossible. This may be illustrated by the following example. The reactions of oxirans with amines are known to occur in polar aprotic solvents, and take place particularly readily in water and alcohols, i.e. under conditions favouring the transition of the nitrogen atom to the sp^3-hybrid state. There is a similar phenomenon also in uncatalysed reactions of oxirans with thiols, the occurrence of which is associated with the presence of hydroxy-compounds in the reaction sphere. In non-polar media, thiols condense with oxirans only in the presence of basic catalysts[275]. Thus one of the characteristics of the nucleophilic oxiran ring cleavage reactions is the necessity to activate the formation of ionic transition complexes, without which the process does not occur under the usual conditions:



In contrast to oxirans, thiirans react smoothly with amines and thiols in non-polar media without catalysts, which suggests that the thiiran ring has more pronounced electrophilic properties than the oxiran ring. The optimal conditions for the formation of monomeric condensation products in these reactions are associated with the creation of conditions for a virtually synchronous formation of a covalent bond between the nucleophilic atom and the ring carbon atom and proton transfer to the sulphur atom. The hydride transfer is mediated by the molecules of the nucleophilic agent, as a result of which the excess of the latter increases the yield of monomeric reaction products:



Consequently, in non-activated nucleophilic ring opening reactions thiirans are distinguished by lower energy barriers to the processes and higher reactivities than oxirans. This is quite natural, bearing in mind the weak bonding and antibonding nature of the C–S σ bond.

The ratio of the rates of the nucleophilic opening of oxiran and thiiran rings changes in polar media. Oxirans react somewhat more readily with amines in dioxan and with thiols in non-polar media in the presence of basic catalysts. In alcohols the opening of the oxiran ring by thiolate anions also takes place quantitatively even below 0°C. In this case thiirans interact on moderate heating. The reversal of the relative reactivities in the above reactions is due to the much smaller sensitivity of thiirans to solvolysis[276] and the impossibility of activating the thiiran ring by the formation of hydrogen bonds. The above facts are intrinsically extremely interesting, since they indicate a definite role of polarisation effects in oxiran and thiiran ring opening reactions.

The energetics of the transition states probably determine the ratio of the reactivities of oxirans and thiirans in electrophilic ring opening processes. This is manifested most clearly in the reactions of the above compounds with phosphorus and arsenic halides. The high rates of reaction of oxirans with phosphorus halides and of thiirans with arsenic halides are attributed to the possibility of the $(n-1)p_\pi - nd_\pi$ interaction between the reacting molecules in the transition complex. A deviation from the above rule is accompanied by a sharp decrease of reactivity. This example demonstrates the impossibility of an unambiguous estimation of the relative reactivities of thiirans and oxirans also in their electrophilic cleavage reactions.

It is noteworthy that, from the standpoint of the chemistry of three-membered saturated heterocycles, the reactivity of thiirans is of special interest. Their low sensitivity to solvolysis, the high lability of the heterobond, and the high polarisability of the heteroatom in thiirans make it possible to discover even fine details of the effects of substituents and of the influence of the structure of the reactants on the reactivity and its nature. Only in the chemistry of thiirans are there so many instances of reactions with the same reactant where all types of transformations of the heterocycle are possible depending on the conditions: elimination of the heteroatom, condensation with formation of monomeric substances, and polymerisation. A detailed elucidation of the nature of this phenomenon is of undoubted interest from the standpoint of the chemistry of three-membered heterocyclic compounds.

The data presented in this review indicate the scope of the synthesis of sulphur-containing substances on the basis of thiirans which has been by no means completely elucidated. However, the known reactions of thiirans already make it possible to obtain by simple technological procedures a wide variety of products of interest for the synthesis of physiologically active and technically valuable compounds. The introduction of these chemically reactive compounds into agricultural practice, into hydrometallurgical processes, and other branches of the National Economy would make it possible to limit the use of stable substances which accumulate in the biosphere and contaminate it.

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Xylitol and Its Derivatives

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The literature data on the pentahydric alcohol xylitol are reviewed. The methods for the preparation of xylitol, its ethers, esters, nitrogen-, halogen-, and sulphur-containing derivatives, acetals, ketals, anhydroxylitols, and their various derivatives are examined and the spectroscopic methods for demonstrating the structures of certain xylitol derivatives are discussed. The therapeutic and diagnostic, dietary, and industrial applications of xylitol and its derivatives are briefly considered. The bibliography includes 553 references.

CONTENTS

I. INTRODUCTION

Until recently xylitol was manufactured on an industrial scale only in the Soviet Union, which has adequate reserves of pentosan-containing raw material. The introduction of xylitol as a commercial product, its physiological activity, and its high reactivity (due to the presence of five free hydroxy-groups) led to its being investigated by chemists, biochemists, and pharmacologists. It rapidly became popular in the food industry, where it began to be used directly, and as a sugar substitute in food products for diabetics. An extensive literature on the chemistry of xylitol, the synthesis of its derivatives, the methods for its analysis, and therapeutic properties exists in various journals, compilations, conference proceedings, and patents. However, so far there has not been even a brief survey of this research.

In the present review the authors attempt to survey the literature data published up to 1974, which makes it possible to assess the advances achieved in the study of the chemistry of xylitol and to outline new promising applications of this polyol.

II. METHODS FOR THE PREPARATION OF XYLITOL

The laboratory and industrial methods for the synthesis of xylitol are based on several of the usual methods in the chemistry of polyols.

The Reduction of Xylose

Syrupy xylitol was obtained for the first time by Bertrand[1] and Fisher[2,3] by the reduction of D- and L-xyloses with sodium amalgam. Aqueous solutions of D-xylose were also hydrogenated in the presence of platinum oxide[4], Raney nickel[5-8], nickel[9] and nickel–cobalt–chromium catalysts on calcium triphosphate[10], nickel on kieselguhr[11,12], nickel–iron carbonate[13] and nickel–copper catalysts on bentonite[14], and titanium–niobium or vanadium–nickel catalysts[15]. Ashida reduced monoses on an aluminium–nickel alloy[16] in non-aqueous solvents: cyclohexanol[15,17,18] and tetrahydrofuryl alcohol[16]. The hydrogenation of aqueous methanol solutions of xylose[19-30] in the presence of Raney nickel and its reduction with aqueous solutions of sodium tetrahydroborate[31,32] and lithium tetrahydroaluminate[33] has been described. Under these conditions, the pentitol was obtained quantitatively from D-xylo-γ-lactone and D-xylityl pentanitrate[34,35].

Karabinos and Ballun[36] developed a convenient method for the preparative synthesis of polyols by the reduction of aldoses and ketoses with Raney nickel. Greighton[10] described an electrochemical reduction of xylose to xylitol. D-Xylitol has also been obtained from 4-*O*-methylglucuronoxylan[37].

Other Methods

Multistage syntheses of xylitol from divinylmethanol[38] and acrolein[39-42] have been described. The oxidation of the terminal glycol group of a hexose or a hexitol followed by reduction yields monoses[43,44] with a smaller number of carbon atoms. 2,4:3,5-Di-*O*-ethylidene-L-xylitol was synthesised in this way from industrial D-sorbitol[45]. Hydrogenolysis of sorbitol[46] yielded a mixture of polyols containing xylitol. Xylitol has been obtained by a microbiological procedure[47-53] and has been isolated from plant material[54-59] and from peat[60,61].

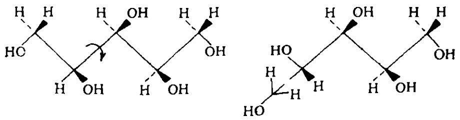
In solutions of anhydrous hydrogen fluoride other pentitols isomerise to xylitol[62,63]. Xylitol derivatives can be obtained by benzoate exchange from sulphonyl derivatives of other pentitols[64].

III. THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF XYLITOL, THE STEREOCHEMISTRY OF XYLITOL AND ITS DERIVATIVES, AND COMPLEX FORMATION

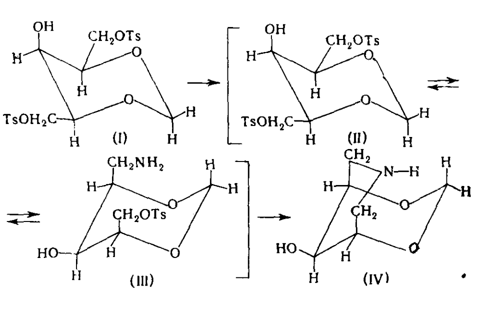
The structure of xylitol was demonstrated by Bertrand[65], Fischer[2,3], and Neuberg[66]. Bertrand obtained 2-iodopentane from xylitol and thus demonstrated the linearity of the hydrocarbon chain and the fact that it consists of five atoms. Fischer and Neuberg oxidised xylitol to DL-xylose and established that this does not entail isomerisation, so that the configurations of the hydroxy-groups of xylitol and xylose are identical. Two crystalline forms of xylitol have been described: a metastable monoclinic form melting at 61–61.5°C,[11,12] which is spontaneously converted into the stable orthorhombic form melting at 94–94.5°C.[12,19,67,68] Apart from two studies[11,12], other instances of the synthesis of the xylitol melting at 61–61.5°C have not been described.

Like other polyols, xylitol is soluble in a limited number of polar solvents: in concentrated sulphuric and hydrochloric acids, water, pyridine, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and hexamethylphosphoramide and to a limited extent in methanol and ethanol. The temperature variation of its solubility in 96% ethanol and water has been studied[69,70], which is important for the technological processes involved in the synthesis of xylitol[7,71–82]. The thermal[83,84], radiation-induced[85], and photochemical[86] degradation of xylitol has been studied. Mai[87] calculated the dissociation constants of the OH groups; the Taft constants and the transport numbers of xylitol in a membrane and in solutions have also been evaluated[88]. The conductometric titration[89] and the cathodic overvoltage in the electrolysis[90] of aqueous xylitol solutions have been investigated.

The reactivities of individual OH groups of unsubstituted xylitol have been scarcely characterised. The synthesis of 1,5-di-*O*-tritylxylitol confirmed the higher reactivity of the primary OH groups[13,91], which is characteristic of all monoses and polyols. Esterification of xylitol by aliphatic C_6–C_{30} acids in the presence of acid and basic catalysts leads to mixtures of monoesters (60–75%) and diesters (20–35%).[92–96] An increase of the temperature of duration of esterification is accompanied by the formation of anhydro-derivatives[93,97,98]. The kinetics and mechanism of the sulphonation reaction have been studied by Yamazaki[99]. It has been found by X-ray diffraction[100] that the xylitol molecule is an asymmetric conformer with a non-planar zig-zag chain owing to the interaction between C_n–O and C_{n+2}–O bonds. Indeed, the study of models showed that interactions via 1,3-bonds lead to rotation about the $C_{(3)}$–$C_{(4)}$ bond with displacement of $C_{(5)}$ from the zig-zag plane[57,101,102]. The distortions of the planar conformer are manifested particularly clearly in the presence of bulky charged substituents, as confirmed by NMR.[103]



It has been suggested that there are no intermolecular hydrogen bonds in the crystals[104].



Some information about the structure of xylitol is provided by the study of complex formation. Xylitol forms complexes with acids, bases and salts. The stable crystalline complex $C_5H_{12}O_5.Ca(OH)_2.4H_2O$ has been described[105]. Copper(II) complexes[106] are used for the analysis and separation of mixtures of polyols. Xylitol forms complexes with boric acid[107,108], with alkali and alkaline earth metal borates[109–111], with cerium(IV) salts[112–114], with pyridine, and with nicotinic and other organic acids[115]. The complexes with iron(III) salts and with citrate[116] are physiologically active. It is believed that the complexes are formed via adjoining OH groups.

The conformations of cyclic acetals of xylitol have been more thoroughly investigated[117]. Danilov and Zarubinskii[118–121] showed that 2,4-*O*-methylenexylitol and its derivatives exist in the *C*-conformations stabilised by the equatorial CH_2OH groups. Presumably the conformation is additionally stabilised by the intramolecular hydrogen bond between the axial $C_{(3)}OH$ group and the oxygen atoms of the acetal ring[122]. The reactivity of the $C_{(3)}OH$ group has been studied and it has been found that in esterification by acid anhydrides the equatorial OH group (*ribo*-configuration) reacts faster, while the axial OH group (*xylo*-configuration) reacts faster with acid chlorides[123]

The formation of an imine when 2,4-*O*-methylene-1,5-di-*O*-tosylxylitol is treated with ammonia[124] should involve an inversion of the conformation. The $C_{(3)}OH$ group in the imine forms part of two rings simultaneously: in one of these it is axial and in the other equatorial, which makes it difficult to interpret the NMR spectra of these compounds.

IV. DERIVATIVES OF XYLITOL

1. Esters (Table 1)

Esters[125–145] are obtained by the usual methods: (1) By esterifying the polyol with an excess of acid, acid anhydride, or an acid chloride in the presence of a catalyst or a base. The first xylitol derivative, the pentaacetate, was synthesised in this way[1,11,32,125–129]. Esterification may be accompanied by the formation of anhydro-derivatives[13,130–133]. For a 1 : 1 ratio of the polyol and the acid, the reaction proceeds with formation of a mixture of a monoester and diesters in proportions of 2 : 1–3 : 1.[92–96,134] (2) By the reduction of the corresponding xylitol derivatives; 2,3,5-tri-*O*-benzoyl-D-[135] and 5-deoxy-5-fluoro-L-xylitols[136] were obtained in this way. (3) With intermediate protection of some of the OH groups. For example, 1-*O*-esters have been obtained by the esterification of di-*O*-isopropylidenexylitol with subsequent hydrolysis of the ketal protecting group[137,138]. Trifluoroacetic acid has been suggested as the hydrolysing agent[144].

Direct interaction with inorganic acids yielded xylityl pentanitrate[32,139–141] (stable below 5°C) and sulphate esters[119,120]. When xylitol is heated with concentrated hydrochloric acid, the product is a mixture of 5-chloro-5-deoxyxylitan as the main component[74]. The interaction of xylitol with phosphorous, hypophosphorous, and phosphonous acid[97,143,145,146] results in the formation of a mixture of xylitol and xylitan derivatives. The structure of cyclic xylitol phosphotriesters[147] has been determined with the aid of the Arbuzov reaction.

2. Ethers

Xylityl ethers are also obtained by standard methods. Interaction with alkyl and aryl halides in the presence of bases yielded 1,5-di-*O*-tritylxylitol[13,91,148], penta-*O*-allylxylitol[149], and trimethylsilyl[150,151] and β-cyanoethyl ethers[152].

Table 1. Esters, ethers, and mixed ether-esters of xylitol.

Name	M.p. (b.p.)/mmHg, °C	References
1-*O*-Octanoylxylitol	59–60	137
1-*O*-Decanoylxylitol	60–64	137
1-*O*-Myristoylxylitol	75–78	137
1-*O*-Palmitoylxylitol	86–88	137
1,2,3,4,5-Penta-*O*-acetylxylitol	62.5–63	11,32,125–129
1,2,3,4,5-Penta-*O*-propionylxylitol	Syrup	132
1,2,3,4,5-Penta-*O*-butyrylxylitol	Syrup	132
1,2,3,4,5-Penta-*O*-lauroylxylitol	33.5–35	132
1,2,3,4,5-Penta-*O*-myristoylxylitol	45.5–47	132
1,2,3,4,5-Penta-*O*-palmitoylxylitol	56–59	132
1,2,3,4,5-Penta-*O*-stearoylxylitol	66–68	132
2,3,5-Tri-*O*-benzoyl-D-xylitol, $[\alpha]_D = 8.5°$ (chloroform)	141–142	135
Penta-*O*-benzoylxylitol	105–106	13,64,135
Tetra-*O*-benzoylxylitol	162–163	13
Penta-*O*-nicotinoylxylitol	185–190	133,481
1-*O*-Methylxylitol	167–169/0.5	119,157
2-*O*-Methylxylitol	Syrup	155
3-*O*-Methylxylitol	Syrup	154
1,4,5-Tri-*O*-methylxylitol	97–99/0.5	157
2,3,4-Tri-*O*-methylxylitol	Syrup	158
1-*O*-Methyl-5-*O*-tritylxylitol	87–88.5	119
2,3-Di-*O*-ethylxylitol	67–68	156
Penta-*O*-allylxylitol	125–127/0.01	149
1,5-Di-*O*-tritylxylitol	152–156	13,91
1,5-Di-*O*-acetyl-2,3,4-tri-*O*-methylxylitol	Not stated	158
2,3,4-Tri-*O*-acetyl-1,5-di-*O*-tritylxylitol	204–206	13,91
2,3,4-Tri-*O*-benzoyl-1,5-di-*O*-tritylxylitol	197–198	13
2,3,4,5-Tetra-*O*-benzoyl-1-*O*-methylxylitol	121–122	157
1,2,3,4,5-Pentakis-*O*-trimethylsilylxylitol	112–113/1	160,162
2,3,4-Tri-*O*-benzyl-1,5-bis-*O*-*p*-nitrobenzoylxylitol	98	153

2,3,4-Tri-*O*-benzylxylitol[153], 2- and 3-*O*-methyl-D-xylitol[154,155], and 2,3-di-*O*-ethyl-D-xylitol[156] were synthesised by reducing xylose derivatives. 1-*O*-Methylxylitol was synthesised from the di-*O*-isopropylidene ketal[119,120,157]. Kochetkov et al.[158] synthesised 2,3,4-tri-*O*-methylxylitol by shortening the chain of D-glucopyranosidouronamide with subsequent reduction of the product. 2-*O*-(4-*O*-Methyl-α-D-glucopyranosyl)-D-xylitol has been isolated from natural products[46] and other similar derivatives have been identified[47,48].

3. Amino-derivatives (Table 2)

1-Amino-1-deoxy-D-xylitol has been synthesised by the reductive amination of D-xylose[159,160] and by the hydrogenation of D-xylose phenylhydrazone[161] or oxime[162]. The bis(phenylhydrazone) of D-threopentulose was reduced similarly to 1,2-diamino-1,2-dideoxy-D-xylitol[163]. Ammonolysis of 2,3-anhydroribose yielded 3-amino-3-deoxyxylitol[164]. Hydrogenation of *N*-amino-D-xylopiperidinose or its dimer, obtained by the acid hydrolysis of 5-deoxy-5-hydrazino-1,2-*O*-isopropylidene-D-xylofuranose, leads to 1,5-imino-1,5-dideoxy-D-xylitol[165,166]. Haskell and Hanessian[167,168] synthesised 5-acetamido-5-deoxy-D- and -L-xylitols from derivatives of iditol mercaptals.

Deamination of 1-deoxy-1-methylaminoxylitol with nitrous acid[169–171] led to 1-deoxy-1-methylnitrosamino-D-xylitol instead of the expected xylitan[172]. Veksler and coworkers[173–176] obtained the quaternary ammonium salts $R\overset{+}{N}(CH_3)_2Alk\overset{-}{Br}$ (R is a xylitol or xylitan residue and Alk is a long-chain $C_{10}-C_{18}$ alkyl group) from 1-deoxy-1-dimethylaminoxylitol by alkylation with alkyl bromides.

Table 2. Nitrogen-containing derivatives of xylitol.

Name; $[\alpha]_D$	M.p., °C	References
1-Amino-1-deoxy-D-xylitol (HBr salt); $[\alpha]_D^{23} = 13°$	167–168	159–162
” (HCl salt)	128–129	159–162
1-Methylamino-	Syrup	172
1-Dimethylamino-	102–104	173
1-Salicylideneamino-	131–133	160,162
1-Decyldimethylammonium (HBr salt)	Amorphous	173
1-Dodecyldimethylammonium- (HBr salt)	145–147	173
1-Dimethylpentadecylammonium (HBr salt)	125	173
1-Hexadecyldimethylammonium- (HBr salt)	88–89	173
1-Dimethyloctadecylammonium- (HBr salt)	89–93	173
5-Acetamido-5-deoxy-D-xylitol; $[\alpha]_D^{23} = +73.2°$	Syrup	168
5-Acetamido-5-deoxy-L-xylitol; $[\alpha]_D^{23} = -41.4°$	Syrup	168
5-Acetamido-5-deoxytetra-*O*-acetylxylitol	Syrup	168
1-Deoxy-1-(methylnitrosamino)xylitol	121–122	169,170,172
1,2-Dideoxy-1,2-bis-salicylideneamino-D-xylitol; $[\alpha]_D^{22} = -106°$	140	163
1,5-Dideoxy-1,5-iminoxylitol (HCl salt)	Syrup	165,166
1,5-Acetimido-1,5-dideoxyxylitol	192–194	165, 166
2,3,4-Tri-*O*-acetyl-1,5-dideoxy-1,5-iminoxylitol	119.5–121	165
Tetra-*O*-acetyl-1-deoxy-1-deoxy-1-methylamino-*N*-nitrosoxylitol	75–76	172
N-Methyl-*N*-tetrahydroxyxylopentylhydrazine- (HCl salt)	116–117	172
N-Benzylidene-*N*-methyl-*N*-tetrahydroxyxylopentylhydrazine	126–127	172
[4-Bis-(2′-chloroethyl)aminobenzylidene]-*N*-methyl-*N*-tetrahydroxyxylopentylhydrazine	143–144	172

4. Deoxy-derivatives (Table 3)

Deoxy-derivatives have also been synthesised by the usual methods of carbohydrate chemistry. Hydrogenation of xylose derivatives yielded 3-acetamido-3,5-dideoxy-D-xylitol[164]. A series of consecutive reactions $RCH_2OH \rightarrow RCH_2OTs \rightarrow RCH_2I \rightarrow RCH_3$[177] or the elimination of sulphur from diethyl mercaptal[178] (R is a xylitol residue) have been used to synthesise 1-deoxyxylitol.

Table 3. Deoxy-derivatives of xylitol.

Name	M.p., °C	References
1-Deoxyxylitol	Syrup	177,178
Tetra-*O*-acetyl-1-deoxy-D-xylitol	62–63	177,178
2-Deoxy-D-xylitol	Syrup	180,181
2-Deoxy-D-tetraphenylcarbamoylxylitol	200–201	180,181
3-Deoxy-D-xylitol	70–71	182,184
3-Deoxy-D-tetraphenylcarbamoylxylitol	205–206	181
Tetra-*O*-benzoyl-3-deoxy-D-xylitol	104	184
3-Acetamido-1,2,4-tri-*O*-acetyl-3,5-dideoxy-D-xylitol	Syrup	164

By shortening the chain of 3-deoxy-D-galactose, a 2-deoxyxylitol derivative was synthesised[179–181]. 3-Deoxyxylitol has been obtained from the epoxides of L-arabinose and D-ribose[182–184].

Hurd and Bonner[185-187] and then Gertsev and Makarov-Zemlyanskii[188] obtained 1,1-deoxy-1,1-di-*C*-phenyl-D-xylitol and its analogues by the *C*-glycosylation of acetyl-β-D-xylose using benzene in the presence of aluminium chloride. Zhdanov and coworkers[189-196] used the organomagnesium synthesis for the same purpose.

Table 4. Thio-derivatives of xylitol.

Name	$[\alpha]_D^0$	M.p. (b.p.)/mmHg, °C	References
1-Thio-L-xylitol	−2.9 (methanol)	170/0.01	199
1-Thio-D-xylitol	+2.4 (methanol)	170/0.01	199
S-Benzyl-1-thio-L-xylitol	+32 (chloroform)	46−59	199
S-Benzyl-1-thio-D-xylitol	−35 (chloroform)	52−63	199
2,3,4,5-Tetra-*O*-acetyl-*S*-benzyl-1-thio-L-xylitol	+11.5 (chloroform)	180/0.01	199
2,3,4,5-Tetra-*O*-acetyl-*S*-benzyl-1-thio-D-xylitol	−12 (chloroform)	180/0.01	199
2,3,4,5-Tetra-*O*-acetyl-*S*-acetyl-1-thio-L-xylitol	+34 (chloroform)	−	199
2,3,4,5-Tetra-*O*-acetyl-*S*-acetyl-1-thio-D-xylitol	−35 (chloroform)	−	199
S-Auro-1-thio-L-xylitol	−	180 (decomp.)	199
S-Auro-1-thio-D-xylitol	−	180 (decomp.)	199
Bis(tetra-*O*-acetyl-*S*-dehydro-1-thio-L-xylitol)	+28 (chloroform)	97−98	199
Bis(tetra-*O*-acetyl-*S*-dehydro-1-thio-D-xylitol)	−28 (chloroform)	97−98	199

5. Thio-derivatives (Table 4)

Stanek and coworkers[199] obtained tetra-*O*-acetyl-1-benzylthio-1-deoxy-L-xylitol from 1,2-*O*-isopropylidene-5-*O*-tosyl-D-xylofuranose, debenzylated it to 1-deoxy-1-thio-L-xylitol, and characterised it in the form of the octaacetyldisulphide and *S*-auro-1-deoxy-1-thio-L-xylitol. Derivatives of the D-series were obtained similarly.

Table 5. Cyclic xylitol acetals and their derivatives. Di- and mono-methylene acetals of xylitol. 2,4 : 3,5-Di-*O*-methylenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
2,4 : 3,5-Di-*O*-methylene-DL-xylitol	201−202	216,217,220
1-Deoxy-D-; +16.5° (chloroform)	154−155	178
1-Deoxy-DL-	155−156	178,216,221
1-*O*-Methyl-	148	286
1-*O*-Acetyl-	156−157	216
1-*O*-Benzoyl-	164−165	216
1-*O*-Tosyl-	145−146	121,216
1-*O*-Methanesulphonyl-	127.5−129	121,216
1-*O*-Chloromethanesulphonyl-	135.5−137.5	121
1-*O*-Phenylcarbamoyl-	196−197	216
Bis-(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)amine	234−240	224
1-Dimethylamino-1-deoxy-	112−113	173−176
1-Amino-1-deoxy-	120−121	224
1-Deoxy-1-dimethyldodecylammonium-1- (bromide salt)	95−94	176
1-Deoxy-1-dimethyloctadecylammonium- (bromide salt)	102−103	176
1-Deoxy-1-dimethylpentadecylammonium- (bromide salt)	116−118	173
1-Deoxy-1-phenylamino-	133	224
1-Benzamido-1-deoxy-	214−215	224
1-Deoxy-1-(*N*-phenyl)toluenesulphonamido-	176	224
1-Deoxy-1-(*N*-phenyl)benzamido-	178	224
1-Deoxy-1-thiocyanato-	147−148	221
1-Chloro-1-deoxy-	129	224
1-Deoxy-1-iodo-	144−145	216
1-*O*-Naphthylcarbamoyl-	211−212	221
Bis-(2,4 : 3,5-dimethylene-Di-xylityl disulphide	192−193	221
NN-Bis(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)benzamide	261−262	224
NN-Bis(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)toluene-*p*-sulphonamide	211−212	224
1-*O*-Allyl-	146	220
1-*O*-Methylallyl-	133−135	220
1-*O*-Methacryloyl-	157	225,237
1-Deoxy-1-methacrylamido-	198	225
1-Deoxy-1-(*N*-phenyl)methacrylamido-	193	224
NN-Bis-(2,4 : 3,5-di-*O*-methylene-DL-xylit-1-yl)-acrylamide	206	225
NN-Bis-(2,4 : 3,5-di-*O*-methylene-DL-ylit-1-yl)-methacrylamide	217	224,225
1-Cinnamamido-1-deoxy-	197−198	225
1-Deoxy-1-α-methylcinnamamido-	193	225
1-*O*-(1′-naphthylcarbamoyl)-	211−212	221
2,4 : 3,5-Di-*O*-methylene-L-xylitol; −25.3°	217−219	43
1-*O*-acetyl-L-; +2.8° (chloroform)	153−154	43
1-*O*-Benzoyl-L-; −23.8° (chloroform)	170−177	215
1-*O*-Tosyl-L-; −2.7° (chloroform)	146−147	176,215
1-Deoxy-1-iodo-L-; −35.9° (chloroform)	166−167	215
2,4-*O*-Methylene-DL-xylitol	108−109	43,119,216
1-*O*-Methyl-	58.5−59	223
1,3,5-Tri-*O*-methyl	84−86	119
1,5-Di-*O*-trityl-	207.5−209	120,124
3-*O*-Methyl-	109−111	124,217
3-*O*-Methyl-1,5-di-*O*-trityl-	230−231	119,124
3-*O*-Acetyl-1,5-di-*O*-trityl	204−206	217
1,3,5-tri-*O*-acetyl-	87−88	216
1,5-Di-*O*-acetyl-3-*O*-methyl-	121−123	217
3-*O*-Acetoxymethyl-1,5-di-*O*-acetyl-	138−139	119,216,226
	139−140	43
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-*O*-methyl-	83−84	223
1-*O*-Tosyl-	128−129	121,221
3-*O*-Tosyl-	134−135	121
1,3-Di-*O*-tosyl	75.5−77.5	121
1,5-Di-*O*-tosyl	122−124	121
1,3,5-Tri-*O*-tosyl	198−199	121,216
3-*O*-Methyl-1-*O*-tosyl	84−85	121
1-*O*-Tosyl-5-*O*-trityl-	146−147	121
3-*O*-Methyl-1,5-di-*O*-tosyl-	137−138	121,124,223
1-*O*-Methyl-3,5-di-*O*-tosyl	114−115	223
3-*O*-Methyl-1-*O*-tosyl-5-*O*-trityl-	162−163	121
3-*O*-Tosyl-1,5-di-*O*-trityl-	89−90	124
3-*O*-Acetyl-1-*O*-tosyl-5-*O*-trityl-	160−162	121
3-*O*-Benzoyl-1-*O*-tosyl-5-*O*-trityl-	194−196	121
3-*O*-Benzoyl-1,5-di-*O*-tosyl-	128−129	223
1,5-Di-*O*-benzoyl-	140.5−141	
3-*O*-Acetyl-1,5-di-*O*-benzoyl-	174−175	121
1,3,5-Tri-*O*-benzoyl	117−118	216
1,5-Di-*O*-benzoyl-3-*O*-methanesulphonyl-	130−132	121
1,5-Di-*O*-benzoyl-3-*O*-tosyl-	140−141.5	121
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-*O*-methane-sulphonyl-	112−118	221
1,5-Di-*O*-methanesulphonyl-	109−110	121
3-*O*-Acetyl-1,5-di-*O*-methanesulphonyl-	134−136	121
1,3,5-Tri-*O*-methanesulphonyl-	152.5−153.5	121
1,3,5-Tri-*O*-chloromethanesulphonyl-	115−117	121
3-*O*-Acetyl-1,5-di-*O*-methanesulphonyl-	134−136	121
1-Deoxy-	52−53	221
1-Deoxy-5-*O*-tosyl-	145−146	221
1-Deoxy-D-; +5.9° (chloroform)	70−72	178
3-*O*-Acetyl-1-deoxy-D-; −5.3° (chloroform)	101−102	178
3-*O*-Acetoxymethyl-5-*O*-acetyl-1-deoxy-D-; −18° (chloroform)	110−111	178
1-Deoxy-5-*O*-tosyl-D-; −2.1° (chloroform)	62−68	178
1-Deoxy-3,5-di-*O*-tosyl-D-; −18.8° (chloroform)	99−100	178
1,5-Dideoxy-5-iodo-3-*O*-tosyl-	123−125	178
3-*O*-Acetyl-1,5-dideoxy-5-iodo-	51−52	178
3,5-Di-*O*-acetyl-1-*O*-chloromethanesulphonyl-	101−109	121
1-Chloro-1-deoxy-3-*O*-methyl-	104−105	217
1-Chloro-1-deoxy-5-*O*-trityl-	203−204	217
3-Acetylmethyl-5-*O*-acetyl-1-chloro-1-deoxy-	141−143	217
1,2,5-Trichloro-1,2,5-trideoxy-3-*O*-methyl-	67−68	217
1-Chloro-1-deoxy-3-*O*-methyl-5-*O*-trityl-	156−157	217
1-Chloro-1-deoxy-3,5-di-*O*-tosyl-	124−125	221
3,5-*O*-Benzylidene-	187−188	221
1-*O*-Acetyl-3,5-*O*-benzylidene-	155−156	221
1-*O*-Benzoyl-3,5-*O*-benzylidene-	173−174	221
3,5-*O*-Benzylidene-1-*O*-tosyl-	149−150	221
3,5-*O*-Benzylidene-1-iodo-1-deoxy-	165−166	221
3,5-*O*-Benzylidene-1-deoxy-	140−141	221
1-Deoxy-3,5-di-*O*-tosyl-	112−113	221
1,3-Anhydro-	104−105	221
1,3-Anhydro-5-*O*-tosyl-	82−83	221
1,3-Anhydro-5-deoxy-5-iodo-	99−100	221
1,3-Anhydro-5-deoxy-	64−65	221
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityl oxalate	159−161	124
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityltoluene-*p*-sulphonate	152−153	124
1,5-Dideoxy-1,5-imino-3-*O*-methylxylityl picrate	230−231	124
1,5-Diamino-1,5-dideoxy-3-*O*-methylxylitol	120	124
1,5-Dideoxy-1,5-diphthalimido-3-*O*-methylxylitol	279−280	124
1,3,5-Tris-*O*-(trimethylsilyl)xylitol	15−16	150
3,5-Anhydro-1-deoxy-2,4-*O*-methylene-D-xylitol; +28.6° (water)	84−85	178
3,5-*O*-Benzylidene-1-deoxy-2,4-*O*-methylene-D-xylitol; +26.3° (chloroform)	160−162	178
3,5-*O*-Methylene-D-xylitol; −16.5° (water)	119−120	218
1,5-Di-*O*-Benzoyl-2,4-*O*-methylene-3-xylulose	115−116	226
2,4-*O*-Methylene-3-xylulose	95.5−97	226

6. Acetals and Ketals (Tables 5–11)

The methods for the synthesis of cyclic acetals and ketals of xylitol and for the demonstration of their structure are well known. Simple empirical rules have been formulated for the formation of acetals[43,200–207], based on the fact that the rings must cause the minimum distortion of the zig-zag polyol chain. It is necessary to consider the stereochemical stability of the molecule as a whole, when the differences between the eclipsed groups C–C/C–H and C–H/C–H and the electrostatic repulsion between the *gauche* C–O/C–O bonds begin to play the main role[208]. The structures of pentitol ketals agree fairly well with these conclusions[209].

The bulk of the groups adjoining the carbonyl groups play a decisive role in the formation of ketals. One of the authors of the review failed to obtain the hexachloroisopropylidene ketal of xylitol under the conditions for the synthesis of trifluoroisopropylidene ketals. The influence of temperature on the reaction has been little studied, although it is known that an increase of reaction temperature accelerates the formation of dioxolans[210,211]. There have been no studies of the role of the solvent, which might form hydrogen bonds[212,213] and thus influence the structure of the product.

Table 6. Ethylidenexylitol and its derivatives; 1,3 : 2,4-di-*O*-ethylidenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
1,3 : 2,4-Di-*O*-Ethylidene-D-xylitol; −3.5° (water)	164–165	45
5-*O*-Benzoyl-D-; −5.0° (chloroform)	155–156	45
5-*O*-Phenylcarbamoyl-D-; +15.7° (chloroform)	215–217	45
5-*O*-Tosyl-	71–74	45
1,3 : 2,4-Di-*O*-Ethylidene-L-xylitol; +5.6° (chloroform)	161–162	227

Table 7. Di- and mono-benzylidenexylitols; 2.4 : 3,5-di-*O*-benzylidenexylitols.

Name; $[\alpha]_D$	M.p., °C	References
2,4 : 3,5-Di-*O*-Benzylidene-DL-xylitol	180–190	1,2,11,17 215,229,230
1-*O*-Methyl-	156–157	119
1-*O*-Allyl-	157	220
1-*O*-Methylallyl-	148–149	220
1-*O*-Acetyl-	179.5–180	215,230
1-*O*-Benzoyl-	173–175	119
1-*O*-Tosyl-	155–157	176,215,236
1-*O*-Methacryloyl-	158	225,237
1-Deoxy-	174	215
1-Deoxy-1-iodo-	207–208	215
1-(2′-Cyanoethyl)-1-deoxy-	140–141	236
1-Deoxy-1-dimethylamino-	154–155	176
1-Deoxy-1-decyldimethylammonium- (bromide salt)	122	176
1-Deoxy-1-dimethyldodecylammonium- (bromide salt)	111	176
1-Deoxy-1-dimethylpentadecylammonium- (bromide salt)	109–111	176
1-Deoxy-1-dimethylhexamethylammonium- (bromide salt)	125	176
1-Deoxy-1-dimethyloctadecylammonium- (bromide salt)	121–122	175,176
1-Butylamino-1-deoxy-	146	224
1-Deoxy-1-piperidino-	166	236
1-(2′-Butylacrylamido)-1-deoxy-	146–147	225
1-(*N*-Butyltoluene-*p*-sulphonamido)-1-deoxy-	126–127	224
2,4 : 3,5-Di-*O*-benzilidene-D-xylitol; −36.9° (pyridine)	187–188	238
1-Deoxy-D-; −34.5° (chloroform)	175–176	178
1-Acetamido-1-deoxy-D-; −38.6° (DMF)	250.5–252.5	238
1,1-Dimethyl-D-; −32.7° (chloroform)	170–173	238
1,1-Diphenyl-D-; +98.8° (chloroform)	183	238
1,1-Diethyl-D-; −25.1° (chloroform)	170–173	238
2,4-*O*-Benzylidene-DL-xylitol	144	231,235
3-*O*-Acetyl-1,5-di-*O*-benzoyl-	128–129	239
1,3,5-Tri-*O*-acetyl-	148–149	42
1,5-Di-*O*-benzoyl-3-*O*-(methylthio)methyl-	160–161	239
2,4 : 3,5-Di-*O*-benzylidene-1-deoxy-D-xylit-1-yl-D-xylitol; −22° (pyridine)	179–180	242
(1-*R*)-1,5-Di-*O*-acetyl-2,4-*O*-benzylidenexylitol 1,3-*O*-Methylene-(1-hydroxy-L-xylitol); +51.4° (chloroform)	160–161	241
(1-*S*)-1,5-Di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-xylitol); 64.6° (chloroform)	144–146	241

Table 8. Di- and mono-acetylsalicylideneacetals; 2,4 : 3,5-di-*O*-acetylsalicylidenexylitols, 2,4-*O*-acetylsalicylidenexylitols, and the corresponding salicylidene acetals of xylitol.

Name	M.p., °C	References
2,4 : 3,5-Di-*O*-acetylsalicylidene-DL-xylitol	219–220	243
1-*O*-Trityl-	159–160	243
1-*O*-Acetyl-	209–210	243
1-*O*-Benzoyl-	205–206	243
1-*O*-Tosyl-	206–207	243
1-Deoxy-	222	243
1-Deoxy-1-thiocyanato-	175–176	243
1-Deoxy-1-iodo-	214–216	243
2,4-*O*-Acetylsalicylidene-L-xylitol	218–219	243
1,3,5-Tri-*O*-acetyl-	126–127	243
2,4 : 3,5-Di-*O*-Salicylidene-DL-xylitol	202–204	244
1-*O*-Trityl-	235–236	244
1-Deoxy-	148–150	243
2,4-*O*-Salicylidene-DL-xylitol	155–156	243

Table 9. Xylitol ketals and their derivatives; di- and mono-isopropylidenexylitols; 2,4 : 3,5-di-*O*-isopropylidenexylitols.

Name; $[\alpha]_D$	M.p. (b.p.)/mmHg, °C	References
2,4 : 3,5-Di-*O*-isopropylidene-DL-xylitol	34–36	5,157,177, 250
1-*O*-Methyl-	78–80/0.5	157
1-*O*-Trityl-	73–75	250
1-*O*-Acetyl-	45–75	177
1-*O*-Benzoyl-	61–62	177,250
1-*O*-Tosyl-	77–78	5,105,177
1-*O*-Octanoyl-	124–126/0.03	137
1-*O*-Myristoyl-	29–30	137
1-*O*-Palmitoyl-	46–49	137
1-*O*-Allyl-	106/0.5	220,245,246
1-*O*-Methylallyl-	154/0.8	220
1-*O*-Methacryloyl-	33–33.5	225,237
1-Deoxy-	88–90/6–7	177
1-Deoxy-1-iodo-	57–59	177
1-*O*-Chloroformyl-	120/09	249
1-*O*-Phenylazobenzoyl-	110–114	249
Bis-(1,2 : 3,4-di-*O*-isopropylidene-DL-xylitol) 5,5′-carbonate	204–206/0.5	249
5-*O*-Fluoroformyl-1,2 : 3,4-di-*O*-isopropylidene-Dl-xylitol	41–42 95/05	249
1,2 : 4,5-Di-*O*-isopropylidenexylitol	Syrup	250
3-*O*-Benzoyl	114–116	64,250
2,3-*O*-Isopropylidenexylitol	145–147/0.5	157
1-*O*-Methyl-	109–111/0.5	157
1,4,5-Tri-*O*-methyl-	69–71/0.5	157
2,3 : 4,5-Di-*O*-isopropylidene-L-xylitol; +12.5°	103–104	157
1,4,5-Tri-*O*-benzoyl-; ? (alcohol)	96–98/0.03	252
1-*O*-Tosyl-; +16.3° (alcohol)	65,66	252
5-*O*-Benzoyl-1,4-dideoxy-2,3-*O*-isopropylidene-D-xylitol; −25.6° (chloroform)	–	253

The resistance of the acetal linkage to acid hydrolysis increases with increase of the negative inductive effect in the acetal group. This has been confirmed by the stability series of the acetal linkages as a function of the acetal group: $(CF_3)_2C > CF_3-C-CH_3 > CH_2 > CH_3CH > (CH_3)_2C \geqslant C_6H_5CH$.

Table 10. Trifluoroisopropylidenexylitols.

Name	M.p. (b.p.)/mmHg, °C	References
2,3 : 4,5-Di-*O*-Trifluoroisopropylidene-DL-xylitol	83-84/0.4	119
1-*O*-Methyl-	79.5-80/0.5	119
1-*O*-Trityl-	105-106	119
1-*O*-Acetyl-; isomer I	104-106	119
isomer II	116-118	119
3-*O*-Methyl-	75-76/0.5	119

Table 11. Cyclohexylidene-DL-xylitols.

Name	M.p. (b.p.)/mmHg, °C	References
2,4 : 3,5-Di-*O*-cyclohexylidene-DL-xylitol	193/0.5	220
1-*O*-Methyl-	183/0.5	243
1-*O*-Trityl-	108	220
1-*O*-Allyl-	152/0.6	220
1-*O*-Methylallyl-	144-147/0.5	220
1-*O*-Tosyl-	86	243
1-Deoxy-1-thiocyanato-	74-75	243
1-Deoxy-	102.5/0.02	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylenexylitol	103-104	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylene-1-*O*-tritylxylitol	182	243
3,5-*O*-Cyclohexylidene-2,4-*O*-methylene-1-*O*-tosylxylitol	153-154	243

The structures of the acetals have been demonstrated by various methods: by selective hydrolysis, chemical modification, and the study of physicochemical constants; for example, the study of the solvolysis constants[214] helped in confirming the *cis*-decalin structure for di-*O*-benzylidenexylitol. It is interesting to note that in the synthesis of this diacetal the monoacetal could not be isolated from the reaction mixture, although it has been stated in the literature that this is possible[157]. Consequently the rate of formation of the second ring greatly exceeds the rate of formation of the first in dibenzylideneacetals of xylitol.

Methyleneacetals. 2,4 : 3,5-Di-*O*-methylenexylitol was obtained for the first time by Ness et al.[43,215] from tri-*O*-methylene-D-sorbitol by selective hydrolysis with subsequent shortening of the chain. The acetal was then synthesised by treating xylitol with formaldehyde[216] or paraformaldehyde[217] in the presence of concentrated hydrochloric acid. Acetolysis of the diacetal leads to 2,4-*O*-methylenexylitol, which does not contain *α*-glycol groups. Schmidt and Nieswandt[218] synthesised 3,5-*O*-methylenexylitol by the selective oxidation of the 1,2-*O*-methylene group in 1,2 : 3,5-di-*O*-methylene-D-xylofuranose to the carbonate group with its subsequent hydrolysis and reduction of the reaction product. This reaction may be of general applicability[219].

Numerous derivatives of di-*O*-methylenexylitol[173,176,220] and mono-*O*-methylenexylitol[119,124,217,221-225] have been obtained. 1,5-Di-*O*-benzoyl-2,4-*O*-methylenexylitol has been oxidised to the corresponding 3-xylulose derivative; it has been shown[226] that this greatly reduces the resistance of the acetal ring to hydrolysis and the free ketose isomerises to a mixture of erythro- and threo-2-ketoses.

Ethylideneacetals. Ness and Fletcher[45] obtained 2,4 : 3,5-di-*O*-ethylidene-L-xylitol by shortening the chain of 1,3 : 2,4-di-*O*-ethylidene-D-sorbitol. Foster et al.[227] synthesised the D-analogue by a similar procedure. The monoacetal derivative has also been obtained[228].

Benzylideneacetals. 2,4 : 3,5-Di-*O*-benzylidenexylitol was obtained for the first time by condensing xylitol with benzaldehyde in the presence of concentrated hydrochloric acid in order to purify the xylitol[1,2]. Its solubility in organic solvents has been determined[229]; it has been shown that the diacetal contains one free OH group[215,230]. 2,4-*O*-Benzylidenexylitol has been synthesised by shortening the chains of 3,5-*O*-benzylidene-D-gluco-D-*gulo*-heptitol[231], 2,4-*O*-benzylidene-D-sorbitol[232], and 2,4-*O*-benzylidene-D-glucuronomercaptal[233] and by the reduction of the diethyl mercaptal of 2,4 : 3,5-di-*O*-benzylidene-D-xylose[234,235].

Various derivatives of the diacetal[119,120,175,176,215,225,236-238] and the monoacetal[228,239] have been described and the kinetics of the esterification of the diacetal have been studied[240]. It has been found that the acetylation of 1,5-di-*O*-benzoyl-2,4-*O*-benzylidenexylitol in DMSO[239] proceeds with formation of methylthiomethyl derivatives. Angyal and James[241] obtained (1*R*)- and (1*S*)-1,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-)xylitol from 2,4-*O*-benzylidene-D-sorbitol. On treatment with aluminium isopropoxide, 2,4 : 3,5-di-*O*-benzylidene-D-aldoxylose gives rise to 2,4 : 3,5-di-*O*-benzylidene-1-deoxy-D-xylit-1-yl-2′,4′ : 3′,5′-di-*O*-benzylidene-D-xylonate via the Claisen–Tishchenko reaction[242].

Acetylsalicylidene- and Salicylideneacetals. Rusanova et al.[243,244] obtained acetylsalicylidene- and salicylidene-acetals by condensing xylitol with the corresponding aldehydes and achieved their interconversion.

Isopropylideneketals. Among the methods for the synthesis of ketals, the condensation of xylitol with acetone in the presence of concentrated sulphuric acid is most frequently used[5,157,245,246]. Derivatives formed via the free OH group have been identified[177,220,225,237,247-249]. It was shown later that the crystalline 2,3 : 4,5-isomer is mainly formed[64,250,251]. An admixture of 10–30% of the 1,2 : 4,5-diketal has been detected by NMR. The isomers have been separated by preparative gas–liquid chromatography (GLC).

A diketal of the L-series has been obtained by shortening the chain of 1,2 : 3,4-di-*O*-isopropylidene-L-iditol[252]. Foster and coworkers[64] converted 1,2 : 4,5-di-*O*-isopropylidene-3-*O*-tosylribitol into 1,2 : 4,5-di-*O*-isopropylidenexylitol by benzoate substitution. Kochetkov and Usov[253] obtained 5-*O*-benzoyl-1,4-dideoxy-2,3-*O*-isopropylidene-D-xylitol from the diethyl mercaptal of 5-*O*-benzoyl-2,3-*O*-isopropylidene-L-arabinose by treatment with methyltriphenylphosphonium iodide.

Trifluoroisopropylideneketals. Zarubinskii and Danilov[119,222] synthesised 2,3 : 4,5-bis-*O*-(trifluoroisopropylidene)xylitol by condensing xylitol and trifluoroacetone in concentrated sulphuric acid solution. The presence of 1,3-dioxolan rings was established in the model derivatives which the above workers obtained: 1,2-*O*-(trifluoroisopropylidene)glycerol and 3-*O*-methyl-1,2 : 4,5-bis-*O*-(trifluoroisopropylidene)xylitol[254]. 1,3-Dioxan rings are characteristic of trifluoroacetone-xylitan derivatives[121]. Thus the condensation of xylitol and trifluoroacetone results in the formation of the 2,3 : 4,5-diketal, consisting of a mixture of several diastereoisomers owing to the non-equivalence of the substituents at the carbonyl carbon atom[254].

Cyclohexylideneketals. Anikeeva and Zarubinskii[220] obtained a diketal containing a primary OH group by condensing xylitol with cyclohexanone[243]. The reaction of 2,4-*O*-methylenexylitol with cyclohexanone led to the synthesis of 3,5-*O*-cyclohexylidene-2,4-*O*-methylenexylitol, which is formed more slowly than di-*O*-cyclohexylidenexylitol. If it is possible to assign a definite structure of the derivative to the rate of its formation[255], then the last diketal is probably a mixture of the 2,3 : 4,5- and 1,2 : 4,5-isomers, by analogy with di-*O*-isopropylidenexylitol.

Table 12. Anhydro-derivatives of xylitol; 1,4-anhydroxylitol and its derivatives.

Name; $[\alpha]_D$	M.p. (b.p.)/mmHg, °C	References
1,4-Anhydro-D-xylitol; −11.2° (water)	160−170/0.02	62
2,3,5-Tri-*O*-acetyl-D-xylitol; +31.5° (dichloroethane)	90−98/0.04	62
2,5-Anhydro-D-xylitol; +10° (water)	150−155/0.2	282
2,5-Anhydro-3,4-di-*O*-tosylxylitol; +33.8° (chloroform)	112−113	281
2,5-Anhydro-1-*O*-benzoyl-3,4-di-*O*-tosylxylitol; +66.6° (chloroform)	141−142	281
2,5-Anhydro-1,3,4-tri-*O*-tosylxylitol; +38.5° (chloroform)	118−119	281
3,4-Di-*O*-acetyl-2,5-anhydro-1-*O*-tritylxylitol; +6° (benzene)	153	282
1,3,4-Tri-*O*-acetyl-2,5-anhydro-D-xylitol; −45.5° (chloroform)	90/0.02	282
1,4-Anhydro-DL-xylitol	140−145/0.01 M.p. 38	259
2-*O*-Methyl-	122/0.8	279
2,3,5-Tri-*O*-ethyl-	Syrup	280
5-*O*-Trityl-	135−137	268
2,3,5-Tri-*O*-allyl-	105−106/0.8	220
2-*O*-Methyl-5-*O*-trityl	124−125	279
3-*O*-Acetoxymethyl-5-*O*-acetyl-2-*O*-methyl-	148−149/2	279
2-*O*-Methyl-5-*O*-tosyl-	71−72	117
2-*O*-Methyl-3,5-di-*O*-tosyl-	104	279
2,3-Di-*O*-acetyl-5-*O*-trityl-	147−148	279
2-*O*-Methyl-3-*O*-tosyl-5-*O*-trityl-	94−95	279
2,3,5-tri-*O*-(trimethylsilyl)-	106	271
2,3-Ethylene-5-*O*-oleoyl-	Syrup	283
3,5-Di-*O*-benzyl-2-*O*-methyl-	58−59	279
2,3-Di-*O*-benzyl-5-*O*-tosyl-	114−116	268
2,3-Di-*O*-benzyl-5-*O*-trityl-	140−142	268
2,3-Di-*O*-acetyl-5-*O*-trityl-	134−135	259
2,3,5-Tri-*O*-benzoyl-	79−80	259
2,3,5-Tri-*O*-(trimethylsilyl)-	90−97/1	150
3,3,5-Triphenylcarbamoyl	193−194	259
3,5-*O*-Thionyl-	83−84	271
2-*O*-Acetyl-3,5-*O*-thionyl-	104−105/0.05	271
2-*O*-Benzoyl-3,5-*O*-thionyl-	96−98	271
3,5-*O*-Thionyl-2-*O*-tosyl-	60−61	271
5-*O*-Hexylphosphonyl-	Syrup	143
5-*O*-Nonylphosphonyl-	Syrup	143
3,5-*O*-Methylene-	83−84.5	271
2-*O*-Methyl-3,5-*O*-methylene-	46−48	286
2-*O*-Ethyl-2,5-*O*-methylene-	90−92/3	287
2-*O*-Hexyl-3,5-*O*-methylene-	84−85/3	287
2-*O*-Decyl-3,5-*O*-methylene-	76−77/3	287
2-*O*-Allyl-3,5-*O*-methylene-	88/1	220
2-*O*-Benzoyl-3,5-*O*-methylene-	113−114	271
3,5-*O*-Methylene-2-*O*-palmitoyl-	61−62	92
3,5-*O*-Methylene-2-*O*-tosyl-	85−86	271
2-*O*-Methacryloyl-3,5-*O*-methylene-	77−78	225,236
2-Deoxy-3,5-*O*-methylene-2-phenylamino-	34−35	224
2-(*N*-Butyltoluene-*p*-sulphonamido)-2-deoxy-3,5-*O*-methylene-	100	224
2-Deoxy-3,5-*O*-methylene-2-phenylamino-	123−124	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylbenzamido)-	128	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylacrylamido)-	103	224
2-Deoxy-3,5-*O*-methylene-2-(*N*-phenylmethacrylamido)-	114	224
3,5-*O*-Ethylidene-	96 − 97	289
3,5-*O*-Ethylidene-2-*O*-methyl-	73/3	289
2-*O*-Benzoyl-3,5-*O*-ethylidene-	103 − 104	289
3,5-*O*-Ethylidene-2-*O*-tosyl-	86	289
3,5-*O*-Ethylidene-2-*O*-methacryloyl-	97 − 98	289
3,5-*O*-Ethylidene-2-*O*-phenylcarbamoyl-	150 − 151	289
3,5-*O*-Benzylidene-	65 − 66	271
3,5-*O*-Benzylidene-2-*O*-methyl-	40 − 41	286
2-*O*-Allyl-3,5-*O*-benzylidene-	157 − 158/0.8	220
3,5-*O*-Benzylidene-2-*O*-benzoyl-	133	271
3,5-*O*-Benzylidene-2-*O*-tosyl-	110	271
3,5-*O*-Benzylidene-2-*O*-methacryloyl-	138	225,237
3,5-*O*-Benzylidene-2-*O*-phenylcarbamoyl-	197 − 198	271,225,237
3,5-*O*-Isopropylidene-	65−66	271
3,5-*O*-Isopropylidene-2-*O*-methyl-	69−70/0.2	286
2-*O*-Allyl-3,5-*O*-isopropylidene-	105−106/0.8	220
2-*O*-Benzoyl-3,5-*O*-isopropylidene-	79.5−80	271
3,5-*O*-Isopropylidene-2-*O*-tosyl-	84	271
3,5-*O*-Isopropylidene-2-*O*-methacryloyl-	56−57	225,237
3,5-*O*-Isopropylidene-2-*O*-phenylcarbamoyl-	107−108	271
3,5-*O*-Cyclohexylidene-	155−158/0.5	271
3,5-*O*-Cyclohexylidene-2-*O*-methyl-	103−104/0.5	286
2-*O*-Allyl-3,5-*O*-cyclohexylidene-	105−106/0.8	220
2-*O*-Benzoyl-3,5-*O*-cyclohexylidene-	104−105	271
3,5-*O*-cyclohexylidene-2-*O*-tosyl-	96	271
3,5-*O*-Trifluoroisopropylidene-	102.5−104	120
2-*O*-Methyl-3,5-*O*-trifluoroisopropylidene-	46.5/0.5	120
2-*O*-Methyl-3,5-*O*-trifluoroisopropylidene-	62−62.5/0.6; M.p.32−34°	120
3,5-*O*-Methylene-2-*O*-polymethacryloyl-	172 (softening)	288
3,5-*O*-Isopropylidene-2-*O*-polymethacryloyl-	136 (softening)	288
5-Chloro-5-deoxy-	48−49	176,269,271
5-Chloro-5-deoxy-2-*O*-methyl-	108−109/2	222
5-Chloro-5-deoxy-2-*O*-methyl-3-*O*-tosyl-	76−77	222
5-Chloro-5-deoxy-3-*O*-methyl-2-*O*-tosyl-	88−88.5	117,197
5-Chloro-5-deoxy-2,3-di-*O*-tosyl-	104	271
2,3-Di-*O*-benzoyl-5-chloro-5-deoxy-	114−115	269
5-Chloro-5-deoxy-2-*O*-tosyl-	95−96	222
5-Chloro-5-deoxy-2(3)-phenylcarbamoyl-	137−138	271
5-Chloro-5-deoxy-2,3-diphenylcarbamoyl-	151−152	271
5-Deoxy-5-fluoro-	117−119/0.02	291
2,3-Di-*O*-benzoyl-5-deoxy-5-fluoro-	72−73	291
5-Deoxy-5-fluoro-2,3-di-*O*-tosyl-	112	291
5-Amino-5-deoxy- (HCl salt)	134	283,292
5-Deoxy-5-ethylamino-	130/1	292
5-Deoxy-5-dimethylamino-	162−165/14	176
5-Deoxy-5-dimethylamino- (oxalate)	72−73	176
5-Deoxy-5-diethylamino-	127/1	292
5-Deoxy-5-phenylamino-	134−135	292
5-Deoxy-5-piperidino-	115−116	292
5-Deoxy-5-dimethylhexadecylammonium- (bromide salt)	98−99	176
5-Deoxy-5-decyldimethylammonium- (bromide salt)	Amorphous	176
5-Deoxy-5-dimethyldodecylammonium- (bromide salt)	90−92	176
(2,3-Di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	146−147	292
N-Ethyl-(2,3-di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	120−121	292
N-Phenyl-(2,3-di-*O*-tosylxylitanyl)toluene-*p*-sulphonamide	141−142	292
5-Deoxy-5-diethylamino-2,3-di-*O*-tosyl-	154−155	292
5-Deoxy-5-piperidino-2,3-di-*O*-tosyl-	130−132	292
1,5-Anhydroxylitol	116−117	276,277
2,3,4-Tri-*O*-acetyl-	122−123	276,277
1,4 : 3,5-Dianhydro-DL-xylitol	77	269,271
2-*O*-tosyl-	114−116	269,271
2-*O*-Methyl-	51/2	269,271
2-*O*-Acetyl-	92/4	271
2-*O*-Benzoyl-	84	271
2-Phenylcarbamoyl-	114	271
2-Phenylamino-	77	274

7. Anhydroxylitols (Table 12)

Mono- and di-anhydro-derivatives of xylitol have been synthesised by two main methods.

Synthesis by intramolecular nucleophilic substitution. The reaction is carried out under acid or alkaline conditions. Various acids are used as the acid catalysts[256−263]. The acid-catalysed conversion of pentitols into anhydro-derivatives leads to the formation of 1,4-anhydro-derivatives, which has been explained by the favourable steric disposition of the OH groups[264]. The anhydro-derivative usually retains the configuration of the initial polyol. However, Hudson and Barker[264] showed that in the presence of acids D-arabitol is converted into the 1,4-anhydro-derivatives of D-arabitol (62.6%), L-ribitol (7.6%), D-ribitol (3.3%), L-xylitol (11.7%), D-xylitol (4.3%), D-lyxitol (6.2%), and L-lyxitol (0.7%). Assuming that the reaction proceeds via an S_N2 mechanism, it is possible to explain the formation of anhydro-derivatives with the D-arabo- and D-lyxo-configurations by the attack of the O^- anionic group at $C_{(2)}$ or $C_{(4)}$ on carbon atoms with primary OH groups and the formation of derivatives with L-xylo- and L-ribo-configurations can be accounted for by the attack of the O^- group at $C_{(1)}$ or $C_{(5)}$ on carbon atoms with secondary OH groups. In the latter case the configuration is inverted. The relative rates of cyclisation increase in the following sequence: lyxitol < arabitol < xylitol < ribitol < 1-deoxy-D-arabitol < 2-deoxy-D-arabitol. Barker[265] determined the rates of conversion of hexitols into 1,4-anhydro-derivatives and arranged them in the following sequence: mannitol < gulitol < galactitol < altritol < sorbitol < iditol < talitol < allitol. In the two series the qualitative dependence of the rate of cyclisation on the configuration of the OH groups at the first four carbon atoms is the same[143,256].

1-Phosphate esters of xylitol readily form xylitans. By treating 1-amino-1-deoxy-ribitol with a mixture of hydrochloric and nitric acids, Kuhn and Wendt obtained ribitan[262]. Similarly 1-deoxy-1-nitrosaminoxylitol can serve as the starting material for the synthesis of xylitan[162]. Similar mechanisms have been proposed for these reactions[258]. Fletcher and coworkers[62] found that ribitan triacetates and tribenzoates form a mixture of ribitan, lyxitan, ribitol, xylitol, and arabitol in liquid HF solution, while the corresponding D-xylitan derivatives give rise to ribitan alone.

A second method for the synthesis of a wide variety of anhydro-derivatives involves intramolecular substitution of sulphonate esters. The reaction proceeds via an S_N2 mechanism and, when the sulphonyl group is attached to a secondary carbon atom, the closure of the oxygen-containing ring proceeds with Walden inversion at this carbon atom. The intramolecular substitution of sulphonates proceeds under the influence of the usual basic agents, although the formation of anhydro-derivatives in an acid medium has also been described[266].

Hartman and Barker[267] determined the characteristics of the formation of anhydro-derivatives for different positions of the tosyl and OH groups. Gray et al.[268] showed that the presence of the benzyloxy-group at the $C_{(4)}$ atom in 1-*O*-tosyl derivatives promotes the substitution of the tosyl group. It is suggested that the reaction involves the formation of an oxonium ion stabilised by the aryl substituent. The rate of cyclisation depends on the configuration of the OH groups responsible for the steric interactions in the transition and ground states.

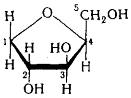
1,3-Anhydro-2,4-*O*-methylenexylitol was obtained by treating 2,4-*O*-methylene-1-*O*-tosylxylitol with an aqueous or aqueous acetone solution of alkali[178,221]. Under the same conditions, the 3-*O*-tosyl derivative remained unchanged[121]. Danilov and Kazimirova[269] and then Wiggins[270] synthesised the 1,4 : 3,5-dianhydroxylitol, the structure of which was established by Ustyuzhanin, Sidorova, and Danilov[197,271,272]. 1,4 : 2,3-Dianhydroxylitol was obtained from 1,4-anhydro-5-chloro-5-deoxy-2-*O*-tosylxylitol[273,274] and 1,4 : 2,5-dianhydroxylitol was synthesised from 2,5-anhydro-3,4-di-*O*-tosyl-D-xylitol[275].

Synthesis by reduction methods. Fletcher and Hudson[276] hydrogenated 2,3,4-tri-*O*-acetyl-D-pyranoxylal or eliminated sulphur from 1-phenylthio-β-D-xylopyranoside triacetate and obtained 1,5-anhydro-2,3,4-tri-*O*-acetylxylitol. The same product was obtained by eliminating sulphur from 1-thio-β-D-xylopyranose[277] or β-D-glucopyranosyl-*NN*-dimethyldithiocarbamate[278] on Raney nickel.

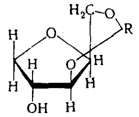
1,4-Anhydroxylitol (xylitan) and its derivatives. Xylitan has been manufactured in the Soviet Union since 1950 and has been studied more thoroughly than other anhydro-derivatives. It was described for the first time by Grandel[260] and Carson and Maclay[259], who isolated crystalline hygroscopic xylitan, melting at 38°C, and showed that it contains one primary and two vicinal secondary OH groups, which confirmed the 1,4-anhydro-structure.

A wide variety of ethers, esters, and thio-derivatives of xylitan are known[62,143,150,163,220,259,268,279-283]. Among the sulphonates of the anhydro-derivative, unsaturated compounds have been synthesised in the presence of DMS solution of KI and zinc dust[281,284,285]. Methylene[92,220,224,225,237,271,286-288], ethylidene[289], and benzylidene[220,225,237,271,286] acetals and isopropylidene[220,224,237,271,286,288], cyclohexylidene[220,271,286], and trifluoroisopropylidene ketals[120] and their derivatives, including polymeric derivatives[289,290], have been described. Halogeno-[117,176,197,222,269,271,291] and amino-derivatives[274,283,292,293] have been obtained.

The structures of cyclic acetals and ketals of 1,4-anhydroxylitol (V) have been studied mainly by the authors of the present review. It has been established[279] that the acetal and ketal groups occupy the same 3,5-positions [compounds (VI)]. Examination of the xylitan model showed that the tetrahydrofuran ring fixes rigidly the *trans*-disposition of the $C_{(2)}-C_{(3)}$ hydroxyls and therefore the formation of acetal and ketal linkages involving these groups is apparently hindered. 1,4-Anhydroribitol, in which there is a *cis*-disposition of the hydroxyls at $C_{(2)}$ and $C_{(3)}$ is known to form 2,3-ketals readily[294].



(V)



(VI)

Danilov and coworkers showed that the second anhydro-ring in 1,4-anhydroxylitol is also formed via the 3- and 5-hydroxyls and the product is therefore 1,4 : 3,5-dianhydroxylitol and not the 1,4 : 2,5-derivative as had been believed previously[269,271,272]. The nucleophilic substitution of the tosyl group at $C_{(2)}$ in dianhydroxylitol proceeds via an S_N2 mechanism with inversion of the configuration at this atom and the formation of lyxitol derivatives[275].

Xylitol derivatives in which the substituent is linked to the polyol molecule via a carbon–carbon bond have been synthesised. These compounds (Table 13), which have been obtained from xylose, do not have an aldehyde group and we have therefore classified them as xylitol derivatives, although in the original studies the authors called them xylose derivatives. For this reason, two names are quoted for these compounds in the Table.

V. PHYSICAL METHODS FOR THE DETERMINATION OF THE STRUCTURES OF CYCLIC ACETALS

The experimental determination of the structures of acetals is usually difficult: in the course of chemical reactions occurring during partial acid hydrolysis, there is a possibility of the isomerisation and migration of the acetal and acyl groups. Hydrolysis is inapplicable to stable rings and the structures of the diastereoisomers of acetals with various groups attached to the carbonyl moiety cannot be determined by purely chemical methods. Numerous studies using model acetals showed that spectroscopic methods are the most promising for the determination of the structures of cyclic acetals. They require small amounts of the test substance, the analysis is carried out under neutral conditions, and both the structure and conformation of the derivative are determined.

Table 13. *C*-Substituted xylitol derivatives.

Name	M.p., °C	References
1-Deoxy-1,1-di-*C*-phenyl-D-xylitol	167–168	185,186
1-Deoxy-*α*-*C*-phenyl-*β*-*C*-*p*-tolylxylitol	163.5–164.5	185,186
2,3,4-Tri-*O*-acetyl-1-*C*-anisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-anisoyl-1-deoxy-D-xylitol)	129.5–130.5	189
2,3,4-Tri-*O*-acetyl-1-*C*-chlorophenyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-chlorophenyl-1-deoxy-D-xylitol)	149.5–150.5	189
2,3,4-Tri-*O*-acetyl-1-*C*-chloroanisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-chloroanisoyl)-1-deoxy-D-xylitol)	151–153	189
2,3,4-Tri-*O*-acetyl-1-*C*-bromoanisoyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-*C*-bromoanisoyl-D-xylitol)	159–160	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-nitroanisoyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-nitroanisoylxylitol)	155.5–156.5	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-phenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-phenethyl-D-xylitol)	130.5–131	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-nitrophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-nitrophenethyl-D-xylitol)	165.5–167	189
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-diphenyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-diphenyl-D-xylitol)	191–192	190
2,3,4-Tri-*O*-acetyl-1-*C*-allyl-1-deoxy-D-xylose (2,3,4-tri-*O*-acetyl-1-*C*-allyl-1,5-anhydro-1-deoxy-D-xylitol)	Syrup	190
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-thienyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-thienyl-D-xylitol)	151–152	190
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-*o*-tolyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-*o*-tolyl-D-xylitol)	110–111	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dibromophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dibromophenethyl-D-xylitol)	80–81.5	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dichlorophenethyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dichlorophenethyl-D-xylitol)	Syrup	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-dibromoallyl-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dibromoallyl-D-xylitol)	123–124	195
2,3,4-Tri-*O*-acetyl-1-deoxy-1-*C*-*dithiocyanatoallyl*-D-xylose (2,3,4-tri-*O*-acetyl-1,5-anhydro-1-deoxy-1-*C*-dithiocyanato-allyl-D-xylitol)	95.5–98	195
1-Deoxy-1-*C*-*β*-indol-D-xylitol	140–145	194
1-Deoxy-1-*C*-hexachlorocyclohexyl-D-xylitol	Syrup	194
1-Deoxy-1-*C*-phenyl-D-xylitol	168–169	188,196
1,5-Anhydro-1-deoxy-1-*C*-phenyl-D-xylitol	148–148.5	187,196
2,3,4-Tri-*O*-benzoyl-1-deoxy-1-*C*-phenyl-D-xylose (1,5-anhydro-2,3,4-tri-*O*-benzoyl-1-deoxy-1-*C*-phenyl-D-xylitol)	168	196

Infrared spectroscopy [295] of acetals and ketals of aldo- and keto-pentofuranoses, aldo- and keto-hexofuranoses, saccharic and uronic acid salts, lactones, and polyols did not reveal the presence of the characteristic bands of 1,3-dioxolans. Bands at 2820–2830 cm^{-1} [296] and at 2770 and 1030 cm^{-1}, [297] which characterise O–C–O stretching vibrations, have been found for 1,3-dioxans. It has been shown that xylitol derivatives with methylene acetal rings [142,255,298] are also characterised by a band in the region of 2800 cm^{-1}. Infrared spectra are used to demonstrate the presence of various functional groups in xylitol derivatives [109,121,217,299] and for the detection of the formation of hydrogen bonds [300].

NMR is used to determine the structures and stereochemistry of the cyclic acetals of monoses and polyols. Evidently 1,2- and 1,3-acetals should be formed in each case in the form of a mixture of two isomers with respect to the positions of the groups at the carbon atom of the acetal bridge. The possibility of the diastereoisomerism of cyclic benzylidene acetals was suggested for the first time by Fischer [301] and later such isomerism was actually observed [162,302,303]. Model substituted and unsubstituted *trans*- and *cis*-5-hydroxy-2-phenyl-1,3-dioxans (benzylidene glycerols) have been paricularly thoroughly investigated [304–314].

The structures of the mono- and di-*O*-acetals of monoses and polyols have been established by ^{1}H NMR. [312,315,316] In particular, the signals of the acetal protons of di-*O*-benzylidenexylitol [317] have been found at τ = 4.79 and 4.85, which confirms the presence of 1,3-dioxan rings with a *cis*-disposition of the groups and the 2,4 : 3,5-structure. The ^{1}H NMR spectra of monomethylenexylityl acetates made it possible to demonstrate the existence of one axial and two equatorial acetyl groups [318].

The proton signals in the NMR spectra of the methyl groups in ketals depend on the relative positions of these groups [266]. This made it possible to show that di-*O*-isopropylidenexylitol is a mixture of two isomers—one giving rise to signals of methyl protons at τ = 8.78 and 8.73 with an intensity ratio of 1 : 3, which corresponds to the 2,3 : 4,5-structure, and another with signals of equal intensity at τ = 8.81 and 8.73 corresponding to the 1,2 : 4,5-structure.

The relation between the structure of the ketal rings and the chemical shift of the fluorine nuclei in trifluoroisopropylidene derivatives has been described [120,121,254,319]. It has been found that the influence of the steric environment on the chemical shift of the fluorine nuclei in the CF_3 group exceeds by a factor greater than 50 the corresponding value for CH_3 groups. These spectra established the quantitative proportions of the diastereoisomers. The NMR and infrared spectra are usually investigated at the same time [118,217,299]. NMR with Fourier transformation yields more information than the proton spectra [320].

VI. METHODS FOR THE ISOLATION AND IDENTIFICATION OF XYLITOL AND ITS DERIVATIVES

Laboratory methods for the column chromatography of xylitol on neutral sorbents [321,323] and the chromatography in aqueous ethanol on ion-exchange resins in salt-forms [323,324] have been described. Ion-exxhange methods are used much more frequently to remove salts from xylitol solutions both in laboratory practice [58,61,325,326] and in industrial manufacturing processes [75,327]. Complexes of xylitol and its derivatives are chromatographed on ion-exchange resins [20,59,328].

Thin-layer chromatography of xylitol and its derivatives [176,329] and GLC of methyl ethers [330], trimethylsilyl derivatives [331–333], trifluoroacetates [333,334], methylated acetates[335], acetates[336], methyl ethers[337], acetals, and ketals[338] are widely used. Methods have been developed for GLC of biological media containing xylitol[329] and for quantitative GLC of polyols with automatic integration of peak areas[340]. Paper chromatography of xylitol[60,341–347] and its derivatives[168,348,349] and molybdate[350] and borate[351] complexes has been used and quantitative paper chromatography of xylitol has been developed[352,353].

Xylitol can be identified on the basis of the mobility of germanate[154], phenylboronate[111,154], and copper complexes in paper electrophoresis[106]. Mass-spectrometric techniques have been developed for the acetates[129,354], methylated acetates[355], methyl ethers[356], benzylidene[357,358] and trimethylsilyl derivatives[359,360], cyclic xylityl phenylboronates[110], and trisaccharides containing xylitol[361]. Xylitol can also be identified by colour reactions[362] and Kofler microscopy[363]. Methods have been proposed for the determination of the OH groups[364]. Quantitative and qualitative analytical methods for xylitol[365] include colorimetric and polarimetric techniques whereby the polyol can be determined in preserved food[366,367] and in atmospheric dust[368].

VII. THE USES OF XYLITOL

1. In Medicine

Studies on the metabolism and clinical applications[369–380], biochemistry, and the mechanism of the action of xylitol[381–383] have been published. It has been shown by the tracer atom method that in the organism xylitol may be formed[383] by the decarboxylation of D-glucuronic acid. The pentosephosphate, glucuronoxylulose[384], and glycerophosphate metabolic cycles[385,386] are thus related.

The lethal dose[387–389] and rational norms for the consumption of xylitol have been determined, since the introduction of excessive amounts of xylitol into the organism entails an increase in weight[388,390,391], although the number of calories produced by xylitol is lower than that produced by glucose[392]. The maximum permissible harmless xylitol contents in water have been established[393]. The intravenous injection of an excess amount of a 10% xylitol solution (in excess of 4.4 g kg^{-1}) produces poisoning symptons[394], which vanish when the administration is terminated. It has been established that the elimination of xylitol from blood is a first-order process[395].

Since it has been found that xylitol increases the level of insulin in animals[371,375,396–415], a detailed study has been made of the physiological action of the polyol on the human organism[416]. A scheme has been proposed for the biosynthesis of proinsulin and insulin in the presence of xylitol[417,418]. Its influence on the carbohydrate and lipid metabolisms of healthy[412,419–424] and sick human beings[420,425–430] of different ages has been investigated. It has been found that xylitol is readily assimilated even by premature and newly born infants[431,432]. Peroral and intravenous administration of xylitol lowers the concentration of lactates[433,434], glucose, and acetoacetic acid in blood and increases the insulin content[394,406,413,422,435–441]. At the same time there is an increase in the amount of glycogen in the liver[377,395], a fall of the level of acetone, and a change in the amount of aminoacids in urine[442].

Xylitol stimulates gastrosecretion[441,443], the biosynthesis of uronic acids[388,444], ATP,[445] corticosteroids hormones[372,373,446,447], proteins[446], and growth hormones[448] and chalcogenetic, choleretic, and pancreatic activities[449–452]. Xylitol has a favourable effect on the functioning of healthy[374,376,444,453,454] and cirrhotic liver[408,409,454,455], reduces haemolysis under the influence of primaquine[365], stabilises the level of bilirubin[388,451], lowers the content of aliphatic acids in the blood[433,439,456,457], stimulates the activity of dehydrogenases[415,458,459], and inhibits isomerases[460]. It is used to inhibit the suppression of adrenocortical activity in hormonal treatment[373,447,461–463]. On the other hand, the introduction of adrenalin suppresses the secretion of insulin caused by xylitol[434]. Thus the effect of xylitol presumably depends on its concentration[451].

It has been found that xylitol is assimilated more slowly than glucose[388], since the organism must become adapted to its assimilation[371,464,465]. Xylitol may serve as a source of energy for cardiac muscle[445,466]. Intravenous administration of xylitol during anaesthesia[467] causes smaller shifts in blood composition than the introduction of glucose. It has been noted the xylitol causes caries to a lesser extent[468], since cariogenic streptococci[389] require a considerable time to become adapted to the assimilation of xylitol[469]. It has been shown that it increases the level of aminopeptidase *B*[469,470] and has a favourable effect during stress[471,472] and in parenteral feeding[394,473–475].

Even prolonged administration of xylitol does not alter the frequency and depth of respiration, arterial pressure, and cerebrocortical activity (up to 1 g kg^{-1})[387] and does not affect the level of uric acid, triglycerides, glycerol, α- and β-lipoproteins, and total cholesterol[424]. D-Xylose or its possible metabolic products, including xylitol, are capable of causing cataract in rats[476].

Xylitol has been recommended for use in gastroenterology[477], in duodenal tubage[450], and in diabetic diets[392,424,478–480]. Cerebral scleroses, hypertonia, and pellagra are treated with xylityl pentanicotinate, which exhibits a vasodilating activity[133,481]. Xylitol derivatives of hydroxycinnamic[482] and 2-hydroxy(acetoxy)-5-iodobenzoic acids[483] exhibit anti-inflammatory activity. Aminoderivatives[228] are analgesics[484].

Xylitol solutions containing hydroxymethylaminomethane are administered intravenously[484] and the xylitol–Fe^{3+}–citrate complex[116], which increases the level of haemoglobin, is administered intramuscularly. Calcium deficiency is compensated by medicinal compositions based on xylitol and calcium carboxylates[485]. The compatibility of xylitol solutions with various combinations of 36 medicinal substances used in infusion has been studied[486]. Quaternary ammonium salts based on xylitol exhibit bacteriostatic activity[173,176]. Xylitol is introduced into ointment bases[487] and into compositions for the pressing of tablets[488].

Methods have been developed for the quantitative determination of xylitol in blood[489,490] and in urine[455], which make it possible to diagnose hepatitis[491] and cirrhosis of the liver[455]. Xylitol is an effective blood preservative, which protects it from haemolysis and the formation of methaemoglobin, reduces methaemoglobin[492–495], and promotes the coagulation of blood[496]. The metabolism of xylitol in erythrocytes has been studied[497]. Xylitol solutions stabilise bacterial cultures in lyophilisation[498] and plant cells in freezing with liquid nitrogen[489,490,499,500]. The latter behaviour is attributed to conformational changes in the plasma–membrane system[501]. Xylitol inhibits[495,502] or promotes[494,503] the germination of various plant seeds.

2. In the Food Industry

Xylitol is being used increasingly to sweeten food products[480,504] together with other synthetic sweetening agents, which are usually employed in low-calorie diets[505]. It is interesting that the maximum sweetness of xylitol is achieved following the addition of 0.06% NaCl; mixtures of xylitol with sodium glutamate, saccharin, and organic acids have been studied[506,507]. Xylitol[504,508] and surfactants based on xylitol and $C_{10}-C_{30}$ aliphatic acids[509], which can be readily blended with dough, are used in the bread baking industry and in preserving fruit[366,510]. Milk with added xylitol has been recommended for the feeding of infants[511]. The taste, colour, bouquet, and stability of alcoholic drinks are improved by the addition of 0.5–3% of xylitol[512].

Xylityl esters of saturated and unsaturated acids[92–96] are relatively non-toxic and can be added in large concentrations (up to 10 wt.%)[509] to food products, in which they serve as dispersing, emulsifying, and surface-active agents. Such esters are soluble in oils, are dispersed in warm water[513], do not cause allergy, and are used as stable non-ionogenic emulsifying agents in cosmetic preparations[131,514–516] and for the stabilisation of food fats[517]. In aqueous solutions xylitol stabilises cysteine[518].

3. In Engineering

Xylitol replaces glycerol as a regulator of foaming[519] and as a plasticiser[520]. In aqueous solutions it protects metals from corrosion[521,522]. Xylitol-containing fluorescent pigments have been prepared[523]. Varnishes, drying oils[524], dyes, adhesives, resins[81,135,182,524–529], wetting and surface-active agents[92–96,134,173–177,228,380,530], non-ionogenic[531] and ionogenic emulsifying agents[173–176], de-emulsifying agents[532–534], polyurethane foam plastics[535,536], film-forming polyurethanes[537,538], polyphthalates[539], and hardening agents for water-soluble polymers[540] are manufactured from xylitol derivatives.

Synthetic tanning agents have been obtained by the condensation of xylityl esters with benzaldehyde and formaldehyde[541] and the condensation of the esters with epoxyethane yielded surfactants with bacteriostatic activity[96]. The product of the electrochemical alcoholysis with xylitol of natural fatty acid triglycerides (linseed oil) is used in the paint and varnish industry[542]. The monoesters of fatty acids and xylitol are employed in dying polyamide fibres[543], in the treatment of viscose staple fibre[544,545], and as deflocculating and flotation agents[137,546,547]. Mixtures of methyl and ethyl ethers of xylitan[548] and mixtures of xylityl esters of resin and tall oil acids[549] have found technical applications. Hardening acrylate oligoesters[550–552], polymethacrylate esters[290], and polycondensation resins[553] have been synthesised on the basis of xylitol.

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Synthesis and Properties of Interpenetrating Networks

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The preparation and the properties of interpenetrating networks are described. Data are reported on the effective density of branch points, and the dependence of viscoelastic characteristics on temperature, proportions of initial components, and mode of preparation. Results are reported for the morphology and mechanical strength indices. The physicochemical properties of interpenetrating networks can be influenced by inorganic fillers previously introduced into one of the components. A list of 35 references is included.

CONTENTS

I. INTRODUCTION

A promising method for modifying the properties of polymers is to prepare mixtures, which may yield materials combining the properties of diverse component polymers. A special place among investigations of such mixtures is occupied by recent studies[1-15] on the production and properties of interpenetrating networks. These are complicated systems comprising two or more three-dimensional network polymers, not chemically combined but inseparable because of mechanical interlocking of chains resulting from the conditions of preparation.

Interpenetrating networks have now been obtained from analogous[1] or chemically related[3] polymers, as well as from systems differing completely in chemical structure and in mode of preparation[6-8]. Thus their preparation can be regarded as a new method for "mixing" not only definitely incompatible but also network polymers, which enables the properties of the latter to be modified. The production of interpenetrating networks from polymers of the most diverse chemical structure is especially promising, since their combination should give materials with a wide range of properties.

II. PREPARATION OF INTERPENETRATING NETWORK POLYMERS

Two methods are available for obtaining interpenetrating networks. The first method consists in swelling a network polymer (first network) in a liquid polymer or oligomer capable of subsequently setting to form a network of a different chemical type (second network) (Fig. 1). Chemical reaction cannot occur between chains of the two network polymers; it is responsible solely for mechanical interlocking of the unlike chains. This method was applied to poly(ethyl acrylate) and polystyrene[2]: the cross-linked polyacrylate (network *1*) was obtained by photopolymerisation in the presence of benzoyl peroxide and diethylene glycol dimethacrylate as cross-linking agent; the resulting sheets were then swollen in styrene with addition of the above initiator and cross-linking agent, and subsequent photopolymerisation gave cross-linked polystyrene (network *2*) embedded in network *1*. Interpenetrating networks were obtained similarly on the basis of poly(ethyl acrylate) and poly(methyl methacrylate) (with tetraethylene glycol dimethacrylate as cross-linking agent)[3,4,12], polystyrene and polybutadiene[15], and also a styrene–divinylbenzene copolymer[1]. In the last case the copolymer was first prepared in the presence of benzoyl peroxide (first network), and specimens were swollen in a mixture of styrene and divinylbenzene with subsequent polymerisation to give a second network embedded in a matrix of the first network of the same nature.

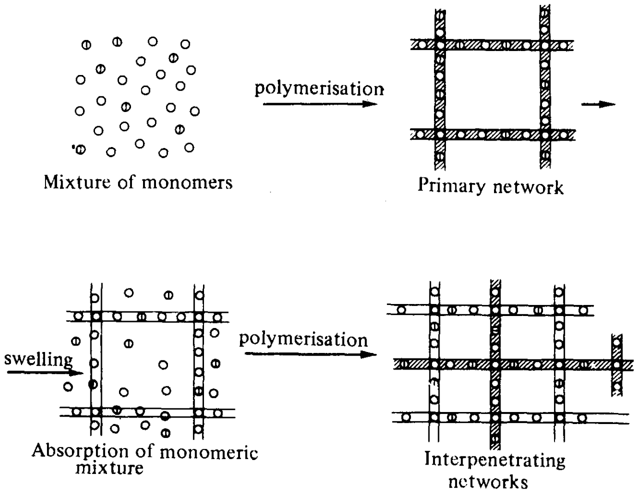

Figure 1. Diagram of first method of generation of interpenetrating networks.

The second method consists in the simultaneous cross-linking of two different polymers already mixed in the same solvent or in suspension. The polymers are selected to ensure mutually independent formation of network structures and to exclude chemical interaction between unlike chains. Frisch et al.[6-10] have used this method to obtain interpenetrating networks consisting of polyurethane based on tolylene di-isocyanate, polyoxypropylene glycol and a polyacrylate, polyurethane and polybutadiene–styrene, and polyurethane and polychloroprene: 50% aqueous emulsions of the polymers containing a cross-linking agent and a stabiliser were stirred vigorously for 1 h, after which films were poured from the resulting composition and kept at a fixed temperature.

The first method of preparation is the more promising, firstly because it permits a more uniform distribution of unlike chains. Secondly, interpenetrating networks can be obtained from the same pair of polymers but with properties varying between wide limits depending on which component is obtained first. This has been shown for cross-linked poly(ethyl acrylate) (network *1*) and a copolymer of styrene with methyl methacrylate (network *2*).[12] If network *1* is synthesised first, and then swollen in a monomer serving as intermediate for the second network, the properties of the resulting interpenetrating networks differ considerably from the "inverse" product obtained when network *2* is synthesised first. We shall discuss the properties of such networks in a later Section.

III. EFFECTIVE DENSITY OF BRANCH POINTS

A fundamental characteristic of the structure of a network polymer is the effective density of branch points, which must therefore first be determined and compared with those in the individual network polymers in order to describe the properties of interpenetrating networks.

Shibayama and Suzuki made such an investigation on interpenetrating networks comprising styrene–divinylbenzene copolymers[1] obtained by the first method to give W_2/W_1 ratios of 1–2 (where W_1 and W_2 are the weights of the first and second networks). The effective density of the network ν_e, determined by means of the equation

$$\nu_e = E/3dRT,$$

where E is the modulus of rubberlike elasticity and d the density of the specimen, was compared with the density of the network ν_T calculated from the ratio of the monomers in first and second networks. Fig. 2 illustrates the dependence of ν_e on ν_T for the first network (line *1*) and for the interpenetrating networks (line *2*). Values of ν_e are evidently higher for the latter, which was attributed[1] mainly to an increase in the number of mechanical contacts on interpenetration of the two networks. The swelling of these specimens in toluene and in acetone was less than those of the individual polymer networks, which confirms the increase in ν_e for the interpenetrating networks. Similar results were obtained by Millar[11] for the same system.

Frisch et al.[6,8,10] have studied the density of cross-linking of interpenetrating networks obtained from chemically different polymers. They determined ν_e by means of the Cluff–Gladding relation[16]

$$\nu_e = \frac{2}{3}\,\frac{h_0 S}{3A_0 RT},$$

where h is the height of the undeformed swollen cylindrical polymer specimen, A_0 its cross-sectional area, S the slope of the linear dependence of the compression of the specimen on the applied stress, R the universal gas constant, and T the absolute temperature. Frisch suggests that, if ν_e for the interpenetrating networks is greater than the arithmetic mean calculated from the ratio of the initial polymers, the networks should exhibit interpenetrability: i.e. he regards ν_e for the mixed system as a measure of the degree of interpenetrability of the networks.

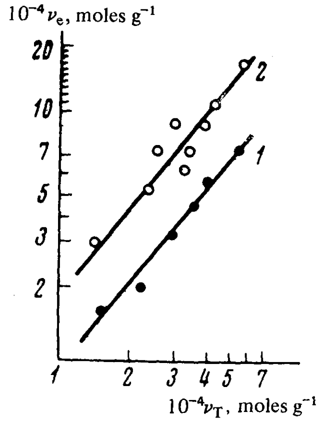

Figure 2. Dependence of ν_e on ν_T for: 1) first network; 2) interpenetrating networks based on styrene–divinylbenzene copolymer.

Table 1. Densities of cross-linking ν_e of interpenetrating networks and of individual components.

System	$10^4\cdot\nu_e$, mole cm^{-3}	Φ_3, %	System	$10^4\cdot\nu_e$, mole cm^{-3}	Φ_3, %
Poly(butadiene-styrene)	0.094	—	Polyurethane + polyacrylate	0.392	9.5
Polyacrylate	0.385	—	Polyurethane + poly-(butadiene-styrene)	0.055	—
Polyurethane	0.350	—	Polyurethane + polychloroprene	0.390	21.9
Polychloroprene	0.306	—	Polyacrylate + poly(butadiene-styrene)	0.342	42.5

The mixed system is considered to comprise three phases—networks *1* and *2* with an intermediate region *3*—the total network density of which is defined as

$$\nu_e = \Phi_1(\nu_e)_1 + \Phi_2(\nu_e)_2 + \Phi_3[(\nu_e)_1 + (\nu_e)_2],$$

where $(\nu_e)_1$ and $(\nu_e)_2$ are the network densities of the individual polymers, and the Φ are the fractions by volume of the different regions, with $\Phi_1 + \Phi_2 + \Phi_3 = 1$. If $\Phi_1 = \Phi_2$, we have $\nu_e = \frac{1}{2}[(\nu_e)_1 + (\nu_e)_2]\,(1 + \Phi_3)$, and therefore $\Phi_3 = [\nu_e - (\nu_e)_0]/(\nu_e)_0$, where $(\nu_e)_0$, the density of cross-linking of the system in the absence of interpenetrability, is given by the arithmetic mean of the ν_e for the individual components. Thus Φ_3 represents the degree of interpenetrability. Table 1 lists values of ν_e obtained by Frisch et al.[6] for the system and for the individual components. In several cases $\Phi_3 > 0$, which suggests interpenetrability, but for the polyurethane–poly(butadiene–styrene) system

$\Phi_3 < 0$, since $\nu_e < (\nu_e)_0$. This is explained by the plasticising action of poly(butadiene–styrene) on the polyurethane network. It was also found that this interpenetrated system swells considerably more than did the individual polymers, which confirms the observed diminution in ν_e relative to the components.

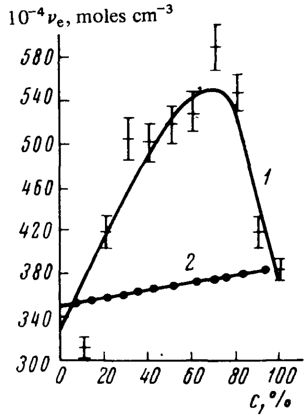

Figure 3. Dependence of effective density of cross-linking of interpenetrating networks on polyacrylate concentration c: 1) experimental; 2) theoretical.

Interesting results on the composition dependence of the density of cross-linking were obtained by Frisch[6] for a polyurethane–polyacrylate system. Fig. 3 shows an extremal dependence of density of cross-linking of the interpenetrating networks on the polyacrylate content. Maximum ν_e is observed at 70% of the latter. The absolute densities of cross-linking are considerably greater than those calculated from the stoichiometric composition. This system will be considered in greater detail in connection with mechanical properties.

IV. EFFECT OF TEMPERATURE ON VISCOELASTIC PROPERTIES

A considerable proportion of research on interpenetrating networks has been concerned with mechanical properties and their temperature dependence. Such an approach provides information on temperature transitions, as well as some indication of the compatibility of the components.

Investigation of the temperature dependence of Young's modulus for the poly(ethyl acrylate)–poly(methyl methacrylate) system[5] has revealed a broad transition region, and dilatometric examination shows also a glass point. Curves representing the variation of the modulus during stretching under creep conditions obtained[4] for the same system show a broad transition region. The range of dispersion of Young's modulus is greater for interpenetrating networks. From the results obtained for this system Sperling suggests that poly(ethyl and methyl methacrylates) are partly compatible components in the formation of interpenetrating networks.

Examination of the relaxation properties of polymer mixtures, e.g. for 50 : 50 mixture of poly(vinyl chloride) and SKN-40 [butadiene–acrylonitrile] synthetic rubber[17], also revealed a single broad transition region.

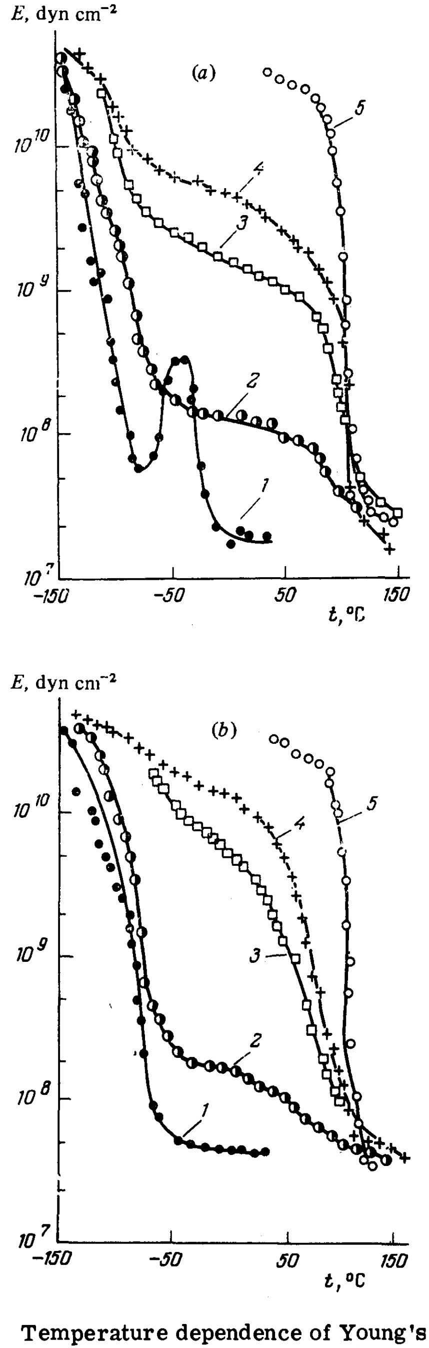

Figure 4. Temperature dependence of Young's modulus for interpenetrating networks containing different quantities (%) of polystyrene: (a) first: 1) 0; 2) 24.4; 3) 61.6; 4) 75.7; 5) 100; (b) second: 1) 0; 2) 25.6; 3) 56.9; 4) 72.4; 5) 100.

Interpenetrating networks based on poly(ethyl acrylate) and polystyrene[2] exhibit different properties from the above system: the temperature dependence of Young's modulus reveals two transitions, corresponding to the respective polymers (at −16 and 75°C). The occurrence of two glass points clearly indicates the formation of two polymer phases in systems of this type. The transition temperatures do not correspond to the glass points of the homopolymers: that of poly(ethyl acrylate) is −22°C, and that of polystyrene 100°C. This was attributed to incomplete phase separation and the existence of an intermediate region in the interpenetrating networks.

Interesting results on the temperature dependence of Young's modulus E were obtained by Sperling for interpenetrating networks based on a crystallising and a non-crystallising homopolymer—respectively polybutadiene and polystyrene—first series[15,18]. A second series of specimens was obtained from non-crystallising polybutadiene with polystyrene. The temperature dependence of the modulus (Fig. 4) reveals for the first series two transition regions, with the glass point corresponding to polybutadiene in the interpenetrating networks higher than in the homopolymer, and that corresponding to polystyrene in the mixed system lower than in the pure polymer. Similar results were obtained for interpenetrating networks based on polystyrene and a polyacrylate.

Incidentally, closer approach of maxima in binary systems was observed when the method of dielectric losses was used to investigate polymers containing polymeric fillers[19], which was attributed to the mutual influence of the components on the molecular mobility of the polymer chains.

Table 2. Incompatibility numbers for first and second series of interpenetrating networks.

Series	Styrene, %	I.N.	Series	Styrene, %	I.N.
First	61.6 75.7	0.81 0.90	Second	56.9 72.4	0.62 0.65

Interpenetrating networks based on crystallising polybutadiene do not crystallise over the temperature range investigated (Fig. 4*a*), exhibiting merely a steeper fall in modulus with temperature than for the second series. The transition ranges are broader in the latter than in the first series. Sperling suggests that the degree of incompatibility should be assessed from the results. He introduces the concept of "incompatibility number (I.N.)", which can be calculated from the temperature dependence of the modulus by means of the equation

$$\text{I.N.} = 1 - \frac{X_1^{-1} + X_3^{-1}}{2X_2^{-1}},$$

where $X = \mathrm{d}(\lg E)/\mathrm{d}T$, the subscripts *1* and *3* correspond to the two transition ranges, and *2* denotes the plateau between the transitions. The incompatibility number varies from zero for a compatible system to unity for an incompatible system. The values listed in Table 2 show that the components of the first series are more incompatible than those of the second series. The reason is that the polybutadiene in the former series crystallises; the possibility of crystallisation or increase in the degree of order in this series tends to increase the incompatibility number.

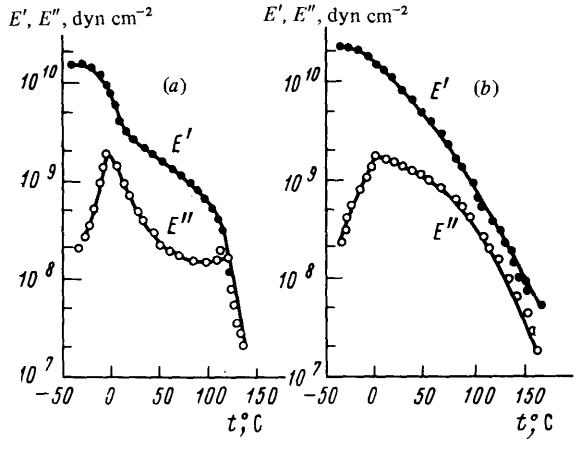

Figure 5. Temperature dependence of E' and E'' for interpenetrating networks of: *a*) 48.8% of poly(ethyl acrylate) plus 51.2% of polystyrene; *b*) 47.1% of poly(ethyl acrylate) plus 52.9% of poly(methyl methacrylate).

Interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene and methyl methacrylate, with tetraethylene glycol dimethacrylate as cross-linking agent, were chosen[13] for the investigation of viscoelastic properties because the components of the copolymer were chemically different and incompatible polymers, while the polyacrylate and the polymethacrylate were partly compatible, as noted above. It was supposed that the degree of compatibility of the interpenetrating constituents would vary considerably with composition. An additional reason for the choice was that polystyrene and poly(methyl methacrylate) have closely similar glass points (100 and 105°C), so that their copolymer would have a similar glass point, which would simplify analysis of the experimental results. Interpenetrated specimens were obtained with different contents of methyl methacrylate in the copolymer and also with different proportions of the constituent polymers, yielding diverse properties. The temperature dependence of the complex modulus of elasticity for the systems based on poly(ethyl acrylate) and polystyrene reveals two transition ranges for both real and imaginary parts E' and E'' (Fig. 5*a*). The transition corresponding to the former polymer is 10 deg above that for the polystyrene homopolymer. In Sperling's view this indicates some molecular compatibility. With interpenetrating systems based on the polyacrylate and the copolymer the peak in the temperature dependence of E'' becomes broader in the copolymer, and the second transition gradually disappears. Interpenetrating systems comprising the polyacrylate and the polymethacrylate exhibit only one transition in the temperature dependence of E' and E'' (Fig. 5*b*), covering a temperature range around 100°C; these results support the earlier conclusion concerning the compatibility of this system.

With a high content of the elastomeric component—poly(ethyl acrylate)—the real part E' drops rapidly after a low-temperature transition (Fig. 6*a*), but with a low content it varies little with temperature (Fig. 6*b*). From this Sperling deduces that the elastomer forms the continuous phase in the first case, whereas the plastic phase is continuous in the second case.

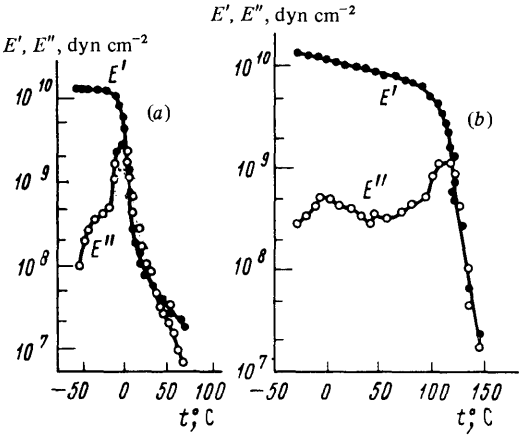

Figure 6. Temperature dependence of E' and E'' for interpenetrating networks of poly(ethyl acrylate) and polystyrene: *a*) 74.4% + 25.6%; *b*) 23.9% + 76.1%.

This worker showed also[13] that the components of the complex modulus and their temperature variation depend on the mode of preparation of the system. The experimental results plotted in Figs. 5 and 6 relate to interpenetrating networks in which the elastomeric part had been synthesised first, and the second network had been polymerised in it (after the monomeric mixture had swollen). But if the second network is prepared first, and then the first network—poly(ethyl acrylate)—is polymerised in it, the resulting "inverse" network exhibits a different temperature dependence of the modulus. The "inverse" system was more rigid than a system obtained by the first method, which indicates the continuity of the polystyrene phase in this network.

Thus investigation of the viscoelastic properties of these systems has shown that those based on poly(ethyl acrylate) and polystyrene are almost incompatible, whereas those comprising the polyacrylate and poly(methyl methacrylate) exhibit considerable miscibility. Materials having different degrees of compatibility are obtained by varying the ratio of the components and the content of the polymethacrylate.

In the investigation of the viscoelastic properties of interpenetrating networks of polyurethane and the polyacrylate, Frisch tried to apply to the results a model developed by Takayanagi[20] for mixtures of polymers. The polyacrylate was regarded as a matrix in which the polyurethane was dispersed. He used the equation

$$E^* = \lambda\left(\frac{\psi}{E^*_{\mathrm{pu}}} \cdot \frac{1-\psi}{E^*_{\mathrm{pa}}}\right)^{-1} + (1-\lambda)E^*_{\mathrm{pa}}$$

in which E^*, E^*_{pu}, and E^*_{pa} are the complex moduli of the system, polyurethane, and the polyacrylate respectively. The parameters ψ and λ are related by the formula $\psi\lambda = \Phi_{\mathrm{pu}}$, the fraction by volume of polyurethane in the system. The closest agreement with the experimental results is obtained by assigning to λ the values 9.45, 0.620, and 0.88, and to ψ the values 0.667, 0.806, and 0.795 for percentage ratios of the polyacrylate to the polyurethane of respectively 70/30, 50/50, and 30/70. The experimental results were satisfactorily described by one of the models developed for mixtures of polymers.

Sperling et al.[13] also showed that the experimental viscoelastic results for the interpenetrating networks were described satisfactorily in terms of Bauer's model[21], in essence a modified Takayanagi model[20]. The applicability of mechanical models developed for mixtures comprising one polymer dispersed in a matrix of another provides additional indirect evidence that interpenetrating networks constitute a two-phase system.

V. MECHANICAL STRENGTH CHARACTERISTICS

In the preparation of interpenetrating networks it is important to compare their mechanical strength indices with those for the individual polymers, and it is also necessary to monitor the variation of these indices with the ratio of the initial network polymers.

Investigation of the strength properties of the systems based on crystallising and non-crystallising polybutadienes with polystyrene (the first and second series above) has shown[18] that a system having a low polystyrene content behaves as a reinforced elastomer, exhibiting high strength and elongation. Increase to 50% of polystyrene is accompanied by an increase in strength to tenfold that of cross-linked polybutadiene. The maximum elongation at rupture is also greater for the interpenetrating networks than for cross-linked polybutadiene. The former are comparable in strength with a block copolymer of styrene and butadiene, but considerably stronger than the random copolymers. The first series are rather stronger than the second series, as a consequence of the ability of polybutadiene in the former to crystallise when stretched. The impact strength of interpenetrating networks having a high polystyrene content exceeds those of a graft copolymer of the same nature and of a styrene homopolymer by factors of 4 and 15 respectively.

The strength properties of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene and methyl methacrylate[13] depend on which network was the first to be obtained. The "inverse" system (with the copolymer obtained first) is considerably stronger than the "straight" system, but maximum elongation at rupture is greater with the latter. Systems of this type, containing a large proportion of the copolymer, have properties almost unaffected by variation in the composition of the copolymer, i.e. by change in the ratio of styrene to methyl methacrylate in it. Such behaviour has been interpreted in terms of the morphology of the networks, as will be described below.

Frisch et al.[6,8] obtained several interpenetrating systems that were usually intermediate in strength between the component networks. In most cases the experimental strength and maximum elongation were smaller than the theoretical values calculated from the composition. The system formed by polyurethane and a polyacrylate was an exception: its experimental strength exceeded the calculated value, and was almost equal to that of pure polyurethane. However, interpenetrating networks of polydimethylsiloxane and a polyacrylate are stronger than either of the component polymers.

Interpenetrating networks of polyurethane and a polyacrylate showed an unexpected variation in strength properties with the content of the latter polymer (Fig. 7): the strength passed at 10% of the polyacrylate through a minimum, and at 75% through a maximum considerably above the strength of pure polyurethane. Frisch attributed the minimum to a decrease in the concentration of hydrogen bonds resulting from introduction of the less polar polyacrylate, which is then functioning as a plasticiser. Subsequent increase in strength is due to a greater number of tangles (contacts) in the system, which tend to "overcome" the diminished concentration of hydrogen bonds. The tangles are assumed to reach a maximum at 75% of the polyacrylate. This is supported by the maximum density of cross-linking at 70% of the polyacrylate (Fig. 3). The density of cross-linking then diminishes, and hence the strength falls. The presence of polyurethane confers great stretchability on this system; in most cases the maximum elongation at rupture determined experimentally exceeds the calculated value.

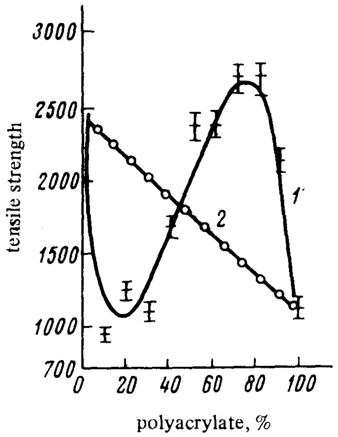

Figure 7. Dependence of tensile strength of interpenetrating networks of polyurethane and a polyacrylate on the content of the latter: 1) experimental; 2) calculated.

The above non-monotonic variation in strength properties and density of cross-linking has been observed in the properties of polyurethanes as functions of the content of inorganic fillers (Aerosil and carbon blacks).[22] In the case investigated by Frisch, the polyacrylate might be regarded as a polymeric filler for the polyurethane. Regarding the properties of interpenetrating networks as those of polymer–polymeric filler systems has been an extremely fertile approach[14], which we shall discuss in detail in connection with the properties of filled interpenetrating networks.

VI. STRUCTURE

Electron-microscopic investigation of the morphology of various types of interpenetrating networks undertaken by Frisch et al. and also by Sperling et al.[12,16] confirms the presence of two polymeric phases deduced from the viscoelastic properties.

Electron micrographs obtained by Frisch et al.[6,8] for a polyacrylate and for polyurethane separately revealed no clearly defined structures, whereas those for the interpenetrating networks exhibited regions differing in optical density, which were regarded as indicating the presence of two phases corresponding to the individual components. Furthermore, the distance between regions of polyurethane embedded in the polyacrylate matrix diminished as the polyurethane content increased from 30% to 50%, and at 70% polyurethane had become the matrix, in which polyacrylate regions were embedded: i.e. inversion had occurred. In this last case the strength was at a minimum (Fig. 7). Increasing the content of the "rigid" phase (the polyacrylate) produces an initial increase in strength, as noted earlier, to reach a maximum at a 70% content. Unfortunately, micrographs were not obtained at higher polyacrylate contents, so that further comparison of the mechanical characteristics with the morphology of the interpenetrating networks is impossible.

Sperling has made an electron-microscopic examination of ultrathin sections of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene with methyl methacrylate[13]. The micrographs reveal a complicated cellular structure with cells of ~ 1000 Å, containing a fine structure with regions of ~ 100 Å. With equal quantities of the polyacrylate and polystyrene, the cell boundaries consist of the polyacrylate, while the intracellular region is filled with polystyrene. With equal quantities of the polyacrylate and of the copolymer, the cell boundaries become less well defined with increase in the content of methyl methacrylate in the copolymer, and the regions of fine structure become larger. When the polystyrene units have been completely replaced by poly(methyl methacrylate), no cellular structure is evident on the micrographs, but the system consists of two phases, exhibiting regions of the polymethacrylate and of the polyacrylate. When the ratio of polyacrylate to copolymer is 75/25, i.e. with elastomeric interpenetrating networks, two polymer phases are observed. Initially, when pure polystyrene enters the system, the dimensions of its regions vary between 800 and 1500 Å, while the polyacrylate particles are 100 Å in diameter. On the introduction of poly(methyl methacrylate) units the copolymer particles contract to 200–750 Å, and a fine dispersion of polyacrylate particles in the polymethacrylate is observed when their ratio is 75/25; no cellular structure is detected. When the ratio of polyacrylate to polystyrene (or the copolymer) is 25/75, the morphology varies little with the content of polystyrene or copolymer having a variable quantity of poly(methyl methacrylate). The cellular structure is considerably less well defined than in the previous cases. The strength characteristics remain practically unchanged in the last case, as noted above.

In all the systems poly(ethyl acrylate)—the polymer formed first—constitutes a matrix in which particles of the second polymer phase are disseminated. However, with inverse systems—in which polystyrene, poly(methyl methacrylate), or a copolymer thereof has been formed first—the matrix is a plastic polymer phase in which are distributed particles of the polyacrylate of mean size 150 Å. Thus the morphology of the system is determined by the network produced first, which forms the matrix. Furthermore, the nature of the matrix governs the mechanical strength parameters: if the matrix is the elastomeric polyacrylate, the system is deformed to a greater extent; conversely, if the rigid component—polystyrene, the polymethacrylate, or the copolymer—was the first to be produced, the resulting system undergoes less deformation.

Investigations of the morphology of polymer mixtures in general have revealed only in certain cases[23] such small particles of polymeric phases (≤ 100 Å) as observed by Sperling for the above systems. This is a specific effect of the first method for obtaining interpenetrating networks, which permits the heterogeneity of the complex system to be diminished. In the second method, used by Frisch et al.,[6,8] considerably larger polymeric phase regions are obtained. These results confirm the above considerations on the advantages of the first method.

Thus the morphological investigations combined with the mechanical properties of the systems indicate that the strength characteristics are determined by the polymer network that forms the matrix. This has been clearly shown by Sperling[12,13] in an examination of the morphological, viscoelastic, and other mechanical properties of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene with methyl methacrylate.

Nevertheless, the morphological investigations support the two-phase character of the systems deduced from the viscoelastic properties. The heterogeneity depends on the composition and the mode of preparation; in some cases it is very slight, as noted above. However, these methods of investigation cannot give a criterion of the true, thermodynamic compatibility of the components. Yet hardly any study has been made of the changes in thermodynamic functions accompanying the mixing of network polymers; a few data only are available on the temperature dependence of heat capacity for interpenetrating networks.

VII. CALORIMETRIC AND SPECTROSCOPIC STUDY

The application by Frisch of differential scanning calorimetry to interpenetrating networks of polyurethane and a polyacrylate indicated some interaction between the component polymers[6]. This method gave glass points for the individual polymers identical with those obtained from mechanical relaxation data. In contrast to dynamic mechanical results, however, a single continuous transition was observed for the interpenetrated system, not two glass points. Frisch explained this by specific features of the two methods: whereas mechanical relaxation involves the movement of chain segments, large units—whole molecules or groups of molecules—must be considered in calorimetric measurements. In other words, the presence of a single glass point indicated by viscoelastic results was attributed by Frisch to compatibility or interpenetration of segments, whereas the presence of a transition established from heat-capacity measurements represented mixing of small groups of molecules. In the opinion of the Reviewers the explanation given by Frisch can hardly be accepted as satisfactory. It is more probable that such divergence in the results obtained by the two methods is due to a difference in their resolving power.

No new absorption bands were detected on the application of infrared spectroscopy to interpenetrating networks of polyurethane and the polyacrylate[6]: only bands characteristic of the individual polymers were observed. Hence chemical interaction does not occur between the mixed three-dimensional systems.

VIII. FILLED INTERPENETRATING NETWORKS

It has been noted above that interpenetrating networks can usefully be regarded as containing a polymeric filler. Investigation of the effective density of branch points in network polymers into which inorganic fillers have been introduced at the stage of formation of the three-dimensional network showed[22] that the network is more imperfect in the presence of the large surface area than when polymerisation occurs in the absence of a filler. The reason is that the strongly developed filler surface at the beginning of the reaction may increase the rate of termination of reaction chains at the surface, with a consequent diminution in the frequency of network formation, which becomes more imperfect. Adsorption of growing polymer chains on the filler surface at later stages in the reaction produces a considerable decrease in their mobility, which affects the rates both of growth and of termination. All this tends to result in a more imperfect structure of the three-dimensional network.

In view of the above considerations the Reviewers have compared[14] the properties of individual network polymers containing inorganic fillers with those of filled interpenetrating networks and of such systems filled with Aerosil introduced into one of the polymers. Polyurethane was the first network, and was then swollen in a mixture of styrene and divinylbenzene with addition of benzoyl peroxide and further polymerisation of the second, copolymer network. Determinations were first made of the densities of the specimens and the effective frequencies of branch points both in the initial components and in the interpenetrated system. The experimental densities were intermediate between those of the individual networks, in agreement with results obtained by some workers[4,6] but contradicting those obtained by Millar[11], who found that the density of the interpenetrating networks had increased relative to those of the initial components. The experimental densities were in several cases, in particular with small W_2/W_1 ratios, less than the additive values. With increase in this ratio and in the filler content the experimental density approaches the theoretical value and then exceeds it, which is especially noticeable at high W_2/W_1 ratios and the maximum filler content.

Flory's method[24] was used for the quantitative assessment of the variation in frequency of interpenetrating networks. Dioxan was used for swelling, since the temperature dependence of the volume fraction v_2 of the polymer in the swollen gel showed that the parameters for interaction of the individual network polymers with this solvent were very closely similar at $\psi \simeq 0.30$. Hence this value can be used to calculate the network frequency in the interpenetrated system. The results listed in Table 3[14] show that the experimental effective network densities ν_e/v are always smaller than the additive values calculated from those of the individual networks.

The effective density of branch points for the system investigated is "intermediate" between those of the individual networks: it exceeds the density of polyurethane and is less than ν_e/v for the copolymer. These results were explained on the basis of the above views and earlier ideas on the structure of filled polymers[25,26]. Interpenetrating networks can be regarded as filled systems in which one of the networks is a continuous network polymeric filler for the other. An attempt can then be made to describe the properties by the effect of a filler on the structure of a network formed in its presence. It had already been established that the structure of a polymer network produced in the presence of a solid surface always

Table 3. Theoretical and experimental values of $10^4\nu_e/v$ for interpenetrating networks of polyurethane (first) and a styrene–divinylbenzene copolymer (second).

Aerosil, %	$10^4\left(\frac{\nu_e}{v}\right)$ Individual networks, expt.			$\frac{W_1}{W_2}$	1% Divinylbenzene			$\frac{W_2}{W_1}$	2% Divinylbenzene			$\frac{W_2}{W_1}$	3% Divinylbenzene		
	first	second +2%	+3% divinylbenzene		$10^4\left(\frac{\nu_e}{v}\right)_{\text{expt.}}$	$10^4\left(\frac{\nu_e}{v}\right)_{\text{theor.}}$	$10^4\frac{\Delta\nu_e}{v}$		$10^4\left(\frac{\nu_e}{v}\right)_{\text{expt.}}$	$10^4\left(\frac{\nu_e}{v}\right)_{\text{theor.}}$	$10^4\left(\frac{\Delta\nu_e}{v}\right)$		$10^4\left(\frac{\nu_e}{v}\right)_{\text{expt.}}$	$10^4\left(\frac{\nu_e}{v}\right)_{\text{theor.}}$	$10^4\frac{\Delta\nu_e}{v}$
0	5.0	14.0	30.0	0.305	5.4	7.0	−1.6	0.283	6.2	7.8	−1.6	0.289	6.6	11.9	−5.3
	—	—	—	0.349	5.1	7.1	−2.0	0.268	5.9	7.9	−2.0	0.308	6.2	12.2	−6.0
0.5	—	—		0.412	4.0	6.1	−2.1	0.175	4.6	6.0	−1.4	0.242	5.0	9.8	−4.8
	4.0	9.0	12.0	0.447	3.9	6.4	−2.5	0.256	4.7	6.3	−1.6	0.240	4.4	9.8	−4.4
								0.305	4.2	6.6	−2.4	0.297	4.5	10.7	−6.2
								0.494	4.7	7.7	−3.0	0.500	4.7	13.7	−9.0
1.0				0.492	5.9	7.5	−1.6	0.289	—	7.8		0.328	5.9	12.3	−6.4
	5.0	10.0	13.0	0.554	5.5	7.5	−2.0	0.462	6.6	8.6	−2.0	0.666	6.2	16.3	−10.1
												2.985	7.1	24.6	−17.5
1.5				0.425	6.3	7.5	−1.2	0.149	6.7	7.0	−0.3	0.14	6.9	8.5	−1.6
	6.0	11.0	18.0	0.498	6.3	7.7	−1.4	0.443	7.2	8.6	−1.4	0.697	6.7	16.4	−9.7
								0.501	7.0	8.9	−1.9				

differs from that of an unfilled polymer: for example, the effective network density of a polymer formed in the presence of a dispersed filler is usually less than the network frequency of the unfilled polymer. In the production of interpenetrating networks the second network, i.e. the styrene–divinylbenzene copolymer, is formed in the presence of an existing first network (polyurethane), i.e. in the presence of a solid surface. As in a filled polymer, therefore, defects may appear here in the network owing to a diminished quantity of chemical branch points and the generation of "free ends" in the network. The effective density of branch points in the second network, formed in the presence of the first network, will therefore be smaller than the frequency of the individual second network.

Nevertheless, chain entanglements are formed during polymerisation, which act as additional network branch points, and hence increase the total density of branch points in the interpenetrating networks. The experimental ν_e/v will be greater or less than the additive value depending on which of the effects predominates, and in some cases equality may be expected. In view of the above considerations the suggestion by Frisch that ν_e/v be regarded as an index of the compatibility of the components in the interpenetrating networks cannot be accepted unreservedly: the components may be partly compatible even when $(\nu_e/v)_{\text{exp}} < (\nu_e/v)_{\text{theor}}$.

Inspection of Table 3 shows also that the difference between experimental and theoretical values of ν_e/v increases with the content of cross-linking agent in the second network, and especially with the content of the latter in the system, i.e. with increase in W_2/W_1. A similar type of variation in ν_e/v is found for interpenetrating networks containing an inorganic filler previously introduced into the first network: the difference between experimental and theoretical values increases with the content of the second network and with its "hardening" resulting from increase in its content of cross-linking agent—divinylbenzene.

Both these factors—increase in the content of divinylbenzene in the second network and increase in the ratio W_2/W_1—tend to increase the number of rigid phenyl groups in unit volume, which prevents formation of chemical branch points in the interpenetrating network and also "hardens" the chain segments between the branch points, preventing formation of physical branch points by the interaction of polar groups. The latter effect is very significant, since it had been established earlier[27] that the proportion of physical links in polyurethane networks is very large. However, the introduction of rigid blocks, as occurs in the system described here, decreases this proportion. All these increase the divergence between experimental and calculated ν_e/v. Thus the effective density of cross-linking of interpenetrating networks is determined by the chemical structure of the initial components and also by their proportions.

Temperature transitions in these systems have been studied by measuring dielectric losses at 300 Hz over a wide temperature range (from −130 to +120°C)[14]. The styrene–divinylbenzene copolymer does not exhibit a maximum value of $\tan\delta$ within this range. Results are therefore reported for the temperature dependence of $\tan\delta$ for the polyurethane network and for the interpenetrating networks with a constant W_2W_1 ratio and different quantities of filler (Fig. 8). A maximum in $\tan\delta$ corresponding to dipole–segmental losses of cross-linked polyurethane (Table 4) is observed at −10°C, and shifts to −4°C on introduction of the maximum quantity of filler, owing to the restriction of segmental mobility of the chains between the branch points of the polyurethane network. This is consistent with effects observed earlier[28].

Increase in the filler content in the interpenetrating networks displaces $\tan\delta_{\max}$ to higher temperatures. A similar effect is produced by increasing the degree of cross-linking in the second network. Thus an analogy can be drawn between the effects of the filler and of rigid blocks of the second network on the molecular mobility of the chains between branch points of the first network. The combined effect of these factors shifts the maximum losses from −10 to 0°C: i.e. a considerable decrease in segmental mobility of the chains occurs between branch points in the first network. The absolute value of $\tan\delta$ is greatly diminished, which also indicates increased chain rigidity in the first network.

A structural investigation of this system was made also under a UEMV-100V electron microscope by the

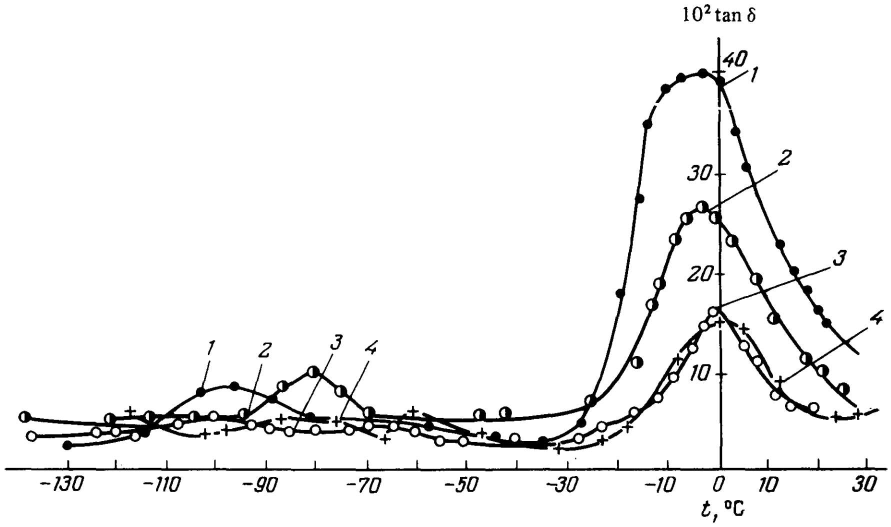

Figure 8. Temperature dependence of tan δ for interpenetrating networks of polyurethane and a styrene–divinylbenzene copolymer for different ratios W_2/W_1 and Aerosil contents (%): 1) 0.3 + 0; 2) 0.3 + 0.5; 3) 0.3 + 1; 4) 0.7 + 1.

Table 4. Dependence of temperature of maximum losses $T_{\max}$ (°C) on quantity of filler in polyurethane (first network) and in interpenetrating networks with $W_2/W_1 = 0.5$.

Aerosil, %	First	Divinylbenzene,		Aerosil, %	First	Divinylbenzene,	
		1%	3%			1%	3%
0.0	—10	—11	—5	1.0	—5	—6	—1
0.5	—3	—9	—3	5,0	—4	—2	0

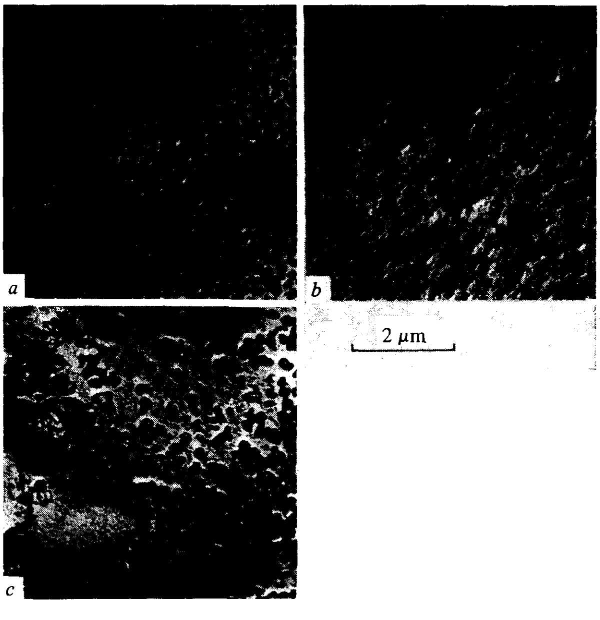

Figure 9. Micrographs of platinum–carbon replicas of the surfaces of: *a*) polyurethane rubber; *b*) styrene–divinylbenzene copolymer; *c*) interpenetrating networks of (*a*) and (*b*).

replica method with preliminary treatment in the oxygen plasma of a high-frequency discharge[29]; the individual networks were also examined. A polyurethane rubber is characterised (Fig. 9*a*) by clearly defined globules of size 0.2 μm and by the presence of interglobular regions. The styrene–divinylbenzene copolymer exhibits smaller globules (0.05 μm), which are considerably less well defined (Fig. 9*b*). Specimens of the interpenetrating networks contain coarser globules (0.4 μm) than in the first network, separated by interstructural regions (Fig. 9*c*). The globules are considerably farther apart than in the first network.

From these results it was concluded that formation of the second network in the presence of the first is accompanied by an increase in the distance between the globules in the latter as the interglobular regions become filled with the copolymer. At the same time the globules themselves become larger (Fig. 9*c*). Thus during swelling of the first network in the mixture of monomers, the latter penetrates not only into the interglobular regions but also into the globules themselves, in which copolymerisation also takes place. Thus introduction of the second network has a significant influence on the structure of the first, leading to increased heterogeneity of the system.

In contrast to the structural investigations made by Sperling and by Frisch, the Reviewers examined[14] the effect of a filler (Aerosil) on the structure of the first network and on the interpenetrating networks obtained from it. Introduction of 1% of Aerosil into polyurethane suppresses the formation of large globules in the first network (Fig. 10*a*), so that the resulting system containing the filler previously introduced into the first of the constituent networks differs from the unfilled system (Fig.

10*b*) in having less clearly defined structural inhomogeneity. Thus the introduction of a filler into interpenetrating networks may change significantly the structure and probably the physicomechanical properties.

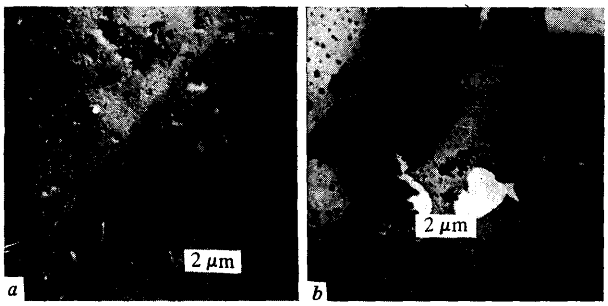

Figure 10. Micrographs of platinum–carbon replicas of surfaces of: *a*) polyurethane rubber filled with 1% of Aerosil; *b*) interpenetrating networks of polyurethane and of a copolymer, filled with 1% of Aerosil, of styrene and divinylbenzene.

The physicochemical and mechanical properties of a polymer are largely determined by the density of packing of the macromolecules. When applied to network polymers, this becomes the density of packing of chain segments between chemical branch points. Any change in intermolecular interactions in the system leads to a change in the density of packing of the macromolecules.

Table 5. Specific surfaces and cohesive energy densities of individual and interpenetrating networks containing various quantities of Aerosil.

Network (W_2/W_1) plus Aerosil	Surface, $m^2\ g^{-1}$	Energy, cal cm^{-3}
First (polyurethane)	24.20	84 ± 1.5
Second (styrene–divinylbenzene)	4.96	95 ± 1.5
Unfilled 0.3	21.10	100 ± 1.5
0.3 + 0.5%	16.12	100 ± 1.5
0.3 + 1%	11.16	–
0.3 + 0.5%	8.37	–
0.66 + 1%	4.03	–
2.98 + 1%	2.03	–
Unfilled 0.443	–	100 ± 1.5

The variation in the porosity of the interpenetrating networks of polyurethane and the styrene–divinylbenzene copolymer, both filled and unfilled, was investigated by the Reviewers[14]. Since the second network is formed in the presence of the already formed first network (filled and unfilled), the process obviously being accompanied by adsorption of growing chains at the surface of the filler and of the first network, changes must be expected in the porosity and other parameters of the polymer.

The variation in the porosity was assessed from the sorption of hexane, which is inert towards the interpenetrating networks, and can thus be used to determine the specific surfaces of these polymers[30,31]. Fig. 11 shows that all the isotherms are sigmoid. The BET equation can be applied to such isotherms to calculate the specific surface, which serves here as a measure of porosity[31]. The calculated results (Table 5) show that the first network has a considerably larger specific surface than has the second. Values for the interpenetrating networks are intermediate between those for the individual networks, but closer to the specific surface of the second network.

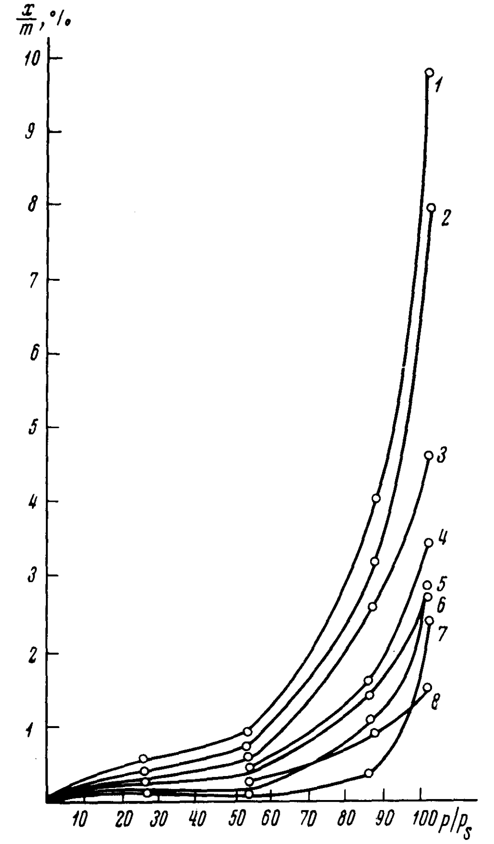

Figure 11. Isotherms for the sorption of hexane vapour by individual and interpenetrating networks with different W_2W_1 ratios and contents (%) of Aerosil: 1) unfilled polyurethane; 2) 0.3 + 0; 3) 0.3 + 0.5; 4) 0.3 + 1; 5) 0.3 + 5; 6) 0.66 + 1; 7) 2.98 + 1; 8) unfilled copolymer of styrene with 3% of divinylbenzene.

The specific surface decreases, i.e. the porosity diminishes, with increase in the ratio W_2/W_1 and in the Aerosil content of the first network. The specific surfaces of the system and of the second network are so small that these polymers can be regarded as non-porous sorbents in Kiselev's classification[32], whereas polyurethane appears as a finely porous sorbent.

Thus entanglements of chain segments of these two networks with a high content of the second network polymer have a considerable effect on the porosity of the system.

This may cause an increase in the density of specimens at high W_2/W_1 ratios, so that the experimental density becomes greater than the theoretical value, as noted above. On the other hand, the density of cohesive energy for the interpenetrating networks is rather greater than those of the individual networks (Table 5). Hence intermolecular interaction is greater in such systems than in the separate networks.

Comparison of the properties of filled and unfilled interpenetrating networks indicates that, if interpenetrating networks are regarded as a filled system in which one component network is a filler for the other, the ideas developed by the Reviewers[22,25,26] on the effect of a filler on the structure of a polymer network can be applied to such systems. We must remember that we are then dealing with a polymeric filler, and must bear in mind that, in contrast to systems with mineral fillers, not only are the properties of the polymer matrix influenced by the filler surface but the properties of the polymeric filler itself also change[19].

The above account shows that the problem of preparing interpenetrating networks and studying their properties is only in an initial stage of development, although the possibilities of the practical application of such materials can already be foreseen. Solution of the fundamental problems of production still lies in the future. In conclusion, therefore, we would like to discuss briefly certain aspects suitable for immediate investigation.

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The primary problem in the synthesis of interpenetrating networks is the mechanism of formation of the second network in the matrix of the first, in view of the chemical and structural heterogeneity of any network polymer[33]. If our model based on the analogy with filled polymer systems is accepted, the matrix will clearly change significantly the conditions of formation of the second network at the interface with the first, and hitherto this has been almost entirely ignored. It is quite obvious that the second network, produced in the first, will never be identical in structure with the network of the same polymer obtained under comparable conditions (of temperature, proportions of components, etc.). Formation of the second network takes place from the very start in the highly viscous medium of the swollen first lattice, i.e. actually under gel conditions. Thus the second network will begin to be formed immediately at the gel point, as it were, but how the gel of the second network will actually be formed, what will be the parameters of this gelation (the extent of reaction at the gel point, the molecular-weight distribution, etc.), is still obscure. By analogy with filled systems the supermolecular structure of the first network will also influence formation of the second network. Therefore additivity of the properties of the two networks cannot in principle be expected: where it is observed, the reasons must be sought.

If the second network is formed by a polymerisation mechanism, chain transfers to molecules of the first network are entirely probable, so that chemical bonding of the two networks is possible even when such bonding should not occur in view of the nature of the two systems. The role of such reactions and the degree of bonding of the networks are still to be elucidated.

The process is complicated also by thermodynamic incompatibility and separation into two phases during formation of the second network. The morphological data reported indicate that the second network is actually formed in interstructural regions of the first, so that structure formation is taking place under complicated conditions. The diagrammatic representation of the structure (Fig. 1), therefore, does not correspond to the actual situation, and perhaps we should speak not of interpenetrating networks but of "parallel" or "coexisting" networks. The structural approach to network formation developed previously[33,34] will therefore be especially fertile.

An important task of research on structure and properties is to establish the effect of the extent of swelling of the first network, the temperature, and the thermodynamics of the "solvent", monomers of the second network, etc. It is necessary also to assess the thermodynamic interaction between the two networks and the possibility of formation of a transition layer and combined supermolecular structures (structural incompatibility), since many properties are determined by the inhomogeneity of the resulting system; as with mixtures of polymers, optimum properties will develop at a certain degree of structural heterogeneity.

Thus we have been the first to detect by reverse gas chromatography the formation of a transition region in interpenetrating networks of polyurethane and a styrene-divinylbenzene copolymer, and have estimated the enthalpy of mixing as a function of the ratio of the networks[35]. However, formation of this region does not indicate compatibility of the component networks, since the experimental enthalpy of mixing was positive. We must therefore speak rather of forced compatibility in such systems. The appearance of a transition region is probably connected with the mechanism of the formation of interpenetrating networks.

Further research is thus required to elucidate specific aspects of the formation and the structure of interpenetrating networks which govern their properties and potential applications.

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Properties of Low Polymers and Their Solutions

V.P.Shaboldin, V.G.Chervin, A.I.Krasheninnikov, and V.N.Demishev

Published information is surveyed on the behaviour of low polymers of diverse chemical structure and on their dilute and concentrated solutions. Consideration is given to the important role of terminal groups, to the influence of the hydrodynamic permeability of a coil on polymer - solvent interaction, to the enhanced mobility of short chains, their flexibility, etc. A list of 108 references is included.

CONTENTS

I. INTRODUCTION

Interest in the properties of polymers with low degrees of polymerisation has recently grown considerably, owing to the importance of their practical applications. These compounds are widely used in the manufacture of polymeric paints, coatings, varnishes, special adhesives, plastic foams, reinforced plastics, thickening additives for lubricating oils, plasticisers, cements and various compositions containing a solid filler, and diverse intermediates[1-4]. Such polymers are also employed in the synthesis of several high polymers. The ability of low polymers to undergo deformation at low shear stresses is exploited to simplify the technology of the production of several polymeric materials.

Thus it is not fortuitous that research papers on them have appeared during recent years. However, the structure and the properties of low polymers and their solutions, in contrast to macromolecular compounds, have been insufficiently studied to date, and published information is fragmentary as to the component composition of the specimens investigated and contradictory as to results. For this reason polymers with low degrees of polymerisation have not yet been fully utilised. Nor has the technology of the production of macromolecular compounds from them been adequately developed.

II. BEHAVIOURAL FEATURES OF LOW POLYMERS AND THEIR SOLUTIONS

The term "oligomers" is applied to compounds of molecular weight below 10 000, whether homogeneous or inhomogeneous in composition. Low polymers occupy a special position, in a transition region between compounds of low and of high molecular weight. The study of short-chain polymers may therefore indicate the molecular weight at which a molecule acquires the properties of a polymer and when a substance can be said to be macromolecular. Low polymer systems and their solutions, while having relatively low molecular masses, possess characteristic rubberlike elasticity[5,6]. Nevertheless, they do not obey many of the rules that have been discovered for high polymers. The past study of the structure of solutions of polymers[7,8] of low molecular weight has been relatively slight, whether theoretical or experimental. Molecular-weight determinations on such polymers and investigation of the properties of their dilute solutions have been accomplished by the modified methods used for high polymers (low-angle X-ray scattering[9], viscosimetry[10], osmometry[11-13]), as well as by methods developed solely for short-chain polymers (cryoscopy and ebullioscopy[14-16], end-group analysis[17], isothermal distillation[18]).

Light scattering provides a most sensitive and accurate method for obtaining reliable information on the structure of macromolecules in dilute solutions[19]. It is interesting in the relative simplicity of the measurements combined with the fairly rapid provision of very accurate data on the conformational properties of macromolecules, size, molecular weight, degree of chain branching, structure-forming processes, etc. However, light scattering can be used to examine polymers only of sufficiently high molecular weight, when the particle size exceeds significantly the wavelength. This method has therefore been regarded as inapplicable to oligomers.

During recent years, in connection with progress in computer techniques, it has become common to investigate model systems of oligomers with computer experiments[20-22], by particular Monte Carlo methods[20-28]. The results obtained for model systems not only provide an idea of the structure of the macromolecule and its behaviour in solution but also permit analysis of earlier theoretical views.

Published information on the properties of low polymers and their solutions shows that, unlike compounds with high degrees of polymerisation, these systems possess several characteristics that cannot be interpreted by the usual theory of polymer solutions: (i) terminal groups of short-chain macromolecules have a significant role, and such macromolecules are able to interact not only among themselves but also with solvent molecules, which may reasonably be expected to influence the shape, size, and permeability of the coil; (ii) these compounds have a transition region of conformations between coil and rod, from compounds of low molecular weight to polymers; (iii) the hydrodynamic permeability of the coil affects polymer-solvent interaction, and the permeability varies with decrease in the length of the macromolecular chain in the transition region; (iv) the effect of long-range interaction diminishes; (v) short chains show enhanced mobility and are capable of orientation and interaction in the field of longitudinal and transverse velocity gradients at low shear stresses; and (vi) oligomers show almost the same capacity for elastic deformation, which is due to the presence of short, flexible chains, relatively unstable intermolecular bonds, and a mobile, fluctuating network. Many investigations have shown that these factors have a significant influence on the hydrodynamic, conformational, thermodynamic, and rheological properties of oligomers.

III. PROPERTIES OF DILUTE SOLUTIONS

The interaction between macromolecules in dilute solutions is divided into short-range and long-range interactions[29], between repeating units respectively comparatively near together and far apart in the polymer chain. Such interactions of units in the same chain are one of the factors responsible for the excluded-volume effect.

One of the main characteristics of a macromolecule in solution is its thermodynamic (equilibrium) flexibility $(\bar{h}_0^2/\bar{h}_{\mathrm{fr}}^2)^{1/2}$, where the $(\bar{h}_0^2)^{1/2}$ are the unperturbed dimensions of the coils, when the effect of long-range interactions is balanced by interaction with the solvent (second virial coefficient $A_2 = 0$), and $(\bar{h}_{\mathrm{fr}}^2)^{1/2}$ are the corresponding dimensions with free rotation of the units in the chain. The dimensions of a macromolecular coil depend on the character of the intra- and inter-molecular interactions, and can be estimated as

$$\alpha_0 = (\bar{h}^2/\bar{h}_0^2)^{1/2},$$

in which α_0 is Flory's coil-swelling coefficient[30] and the $(\bar{h}^2)^{1/2}$ are the dimensions of the coil in an actual solvent.

For oligomers little experimental study has been made of the effects of the nature of the solvent and of the degree of polymerisation on the dimensions of the coil and its properties. Coil size and shape have been determined by optical and viscosity measurements in studies of the properties of dilute solutions of low polymers[9,10,31-35]. Tsvetkov, Frisman, et al.[33-35] examined the dependence of the intrinsic dynamic birefringence on the molecular weight of polyoxypropylene glycols and polystyrene of low molecular weights. From the results the persistent lengths of macromolecules of the oligomers and the molecular-weight dependence of the intrinsic viscosity could be determined. In an investigation of the properties of dilute solutions of polyurethanes and of butadiene–acrylonitrile rubbers of low molecular weight in various types of solvents use of the Stockmayer–Fixman theory enabled the dimensions and the swelling coefficients of real coils to be determined and the flexibility of the macromolecular chain to be estimated by light scattering[10,31,36]. The depolarisation factor, characterising the form of a macromolecular coil of polypropylene glycol, was investigated[32] as a function of the molecular weight and the concentration of the polymer by the use of light scattering. The low-angle scattering of light and of X-rays was used[9] not only to determine the molecular weight and the shape of macromolecules of cellulose nitrate with low molecular weight but also to establish the presence in dilute solution of association complexes, which break down with time.

In contrast to these fragmentary results, a considerably larger number of theoretical studies have been made on the conformational properties of oligomer macromolecules, e.g. on the effect of terminal groups[37,38] (to which a significant role was assigned, in contrast to high polymers). However, conclusions reached from different theories are often mutually contradictory. Experimental results cannot be used for an objective assessment of theoretical predictions, since an exact analytical relation between the measured parameters and the conformations of the macromolecules is lacking. In this situation the application of modern computer experiments and numerical methods has permitted a close approach to solving important problems in connection with the properties of the macromolecules of oligomers.

The majority of results obtained by the Monte Carol method in computer experiments have led to a dependence of the mean distance between end-groups h_{N} and the mean radius of inertia R_{N} on the number of segments N of the form

$$\langle h_N^2\rangle = AN^{Y_n}; \tag{1}$$

$$\langle R_N^2\rangle = BN^{Y_R}, \tag{2}$$

where A, B, Y_{n}, and Y_{R} are empirical constants. The results in most papers lead to the condition $Y_{\mathrm{n}} = Y_{\mathrm{R}} = Y = 1.2$ for all lattices. Simulation by a continuum[28] gives $Y_{\mathrm{n}} \neq Y_{\mathrm{R}}$, which shows that representation of $\langle h_{\mathrm{N}}^2\rangle^{1/2}$ as a multiple of $\langle R_{\mathrm{N}}^2\rangle^{1/2}$ is not always correct: these parameters increase at different rates with increase in the degree of polymerisation. Equations (1) and (2) were deduced from the condition that the interaction potential of the segments is represented by a rigid sphere:

$$\Phi(r) = \begin{cases} 0, & r > d; \\ \infty, & r < d, \end{cases} \tag{3}$$

where r is the distance between the centres of the segments and d is the sum of their van der Waals radii. The functional dependence (1) and (2) is preserved for interaction between segments of a different type, but Y_{n} and Y_{R} vary with $\Phi(r)$. With increase in the energy of attraction the index Y_{n} decreases, to reach unity at some $\Phi(r)$ (the θ point). Equations (1) and (2) are inapplicable in worse solvents than the θ solvent. The interesting result was also obtained that the θ conditions do not correspond to a single point but occupy a region in which most of the conformational parameters, e.g. $\langle h_{\mathrm{N}}^2\rangle$ and $\langle R_{\mathrm{N}}^2\rangle$, assume their own θ values. Computer methods yielded

$$\alpha_N^2 = \langle h_N^2\rangle/N; \tag{4}$$

$$\alpha_{j,N}^2 = \langle h_{j,N}^2\rangle/j, \tag{5}$$

where α_{N}^2 and $\alpha_{\mathrm{j,N}}^2$ are the increases in the distances respectively between the terminal segments and between segments separated by j other segments in a macromolecule comprising N segments. The method of dimerisation was used[39] to construct chains containing up to 4096 segments. Values of $\alpha_{\mathrm{j,N}}^2$ were calculated for $j = 16, 32, \ldots, \frac{1}{2}N$. The results showed that

$$\alpha_N^2 \propto N^{1/5}, \tag{6}$$

as suggested by Flory[30], and that the relation

$$\alpha_N^3 - 1 \propto N^{1/2}, \tag{7}$$

which follows from Fixman's theory[40], is incorrect.

Knowledge of the coordinates of each segment for the whole time of a computer experiment permits not only calculation of the quantities of Eqns. (4) and (5) but also determination of the number of various types of contacts

$$E = E_{ll} + E_{lm} + E_{mm} \tag{8}$$

between segments of the same and different macromolecules in solution, where E_{mm}, E_{lm}, and E_{ll} are the numbers of intramolecular contacts between respectively internal, terminal and internal, and terminal segments. An analogous expression can be written for the number of intermolecular contacts k between macromolecules. Fig. 1 illustrates the dependence of the number of the various types of contacts on the degree of polymerisation P found in a computer experiment. For a model of a macromolecule based on a simple cubic lattice the variation in the total number of intramolecular contacts was given[41] as

$$E = 0.292 \cdot P - 1.15. \tag{9}$$

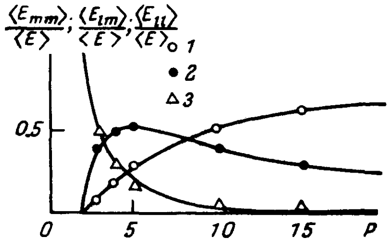

Figure 1. Dependence of number of polymer–polymer contacts on the degree of polymerisation P for a model based on a simple cubic lattice: 1) $\langle E_{mm}\rangle / \langle E\rangle$; 2) $\langle E_{lm}\rangle / \langle E\rangle$; 3) $\langle E_{ll}\rangle / \langle E\rangle$.

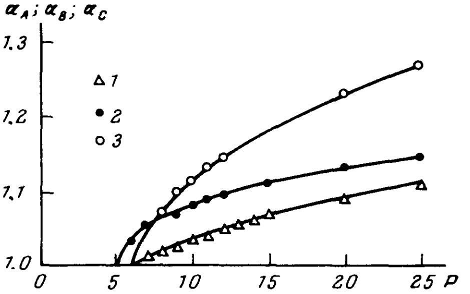

Figure 2. Dependence of coefficients of expansion on degree of polymerisation for a model based on the graphite lattice: 1) α_A (poor solvent); 2) α_B (good solvent for terminal groups); 3) α_C (good solvent for internal groups).

(*a*) Effects of Terminal Groups and of Coil Permeability on Hydrodynamic Properties

Fig. 2 illustrates the dependence of the coefficient of expansion of the macromolecule on the degree of polymerisation and the quality of the solvent, obtained by the Monte Carlo method. This experiment clearly reveals the effect of terminal groups and their relationship to the solvent. The coefficient of expansion always increases with the degree of polymerisation, but most rapidly in a good solvent for terminal and internal segments.

The Mark–Kuhn–Houwink equation[42,43]

$$[\eta] = KM^a$$

expresses the relation between the intrinsic viscosity $[\eta]$, from which the hydrodynamic volume of the coiled macromolecule in dilute solution is estimated, and its molecular weight M, where K and a are constants for a given homologous series. The parameter a, representing the form and the density of the coil, depends on the nature of the solvent and on the hydrodynamic interaction within the space of the coil, and varies mainly from 0.5 to 1. Experimental study of this dependence for several oligomers has established that, for a series of polymer–solvent systems, a decreases as the molecular weight diminishes: i.e. the dependence of $\lg[\eta]$ on $\lg M$ is non-linear (Fig. 3).

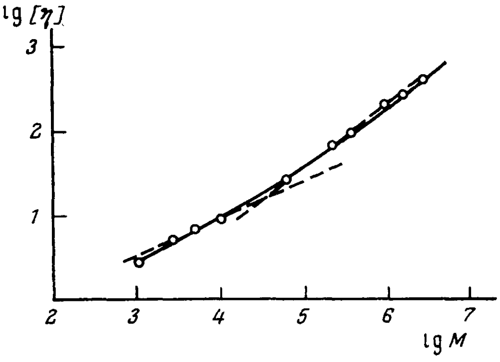

Figure 3. Dependence of $\lg[\eta]$ on $\lg M$ for poly(methyl methacrylate) in benzene at 30°C.

Thus it was shown, for the binary systems formed by benzene with poly(methyl methacrylate)[44] and by water with polyethylene glycol[45], that a is independent of the nature of the solvent for small molecular weights, and is close to 0.5 (which is characteristic of a θ solvent). A possible explanation is that the swelling coefficient α_0 approaches unity in the absence of θ conditions: i.e. long-range interactions are absent. This contradicts all existing theories of solutions, which predict that $\alpha_0 = 1$ only at the θ point with either the second virial coefficient A_2 or the molecular weight approaching zero. The results indicate also that, with decrease in chain length in macromolecules of these oligomers, a small hydrodynamic permeability appears, which is typical of macromolecules under θ conditions. This effect can be attributed to the possibility of interaction between end-groups of small macromolecules, which will change the form of the coil, by decreasing its dimensions (making it more compact), which explains the diminished viscosity.

Several other studies[16,46–49], on oligourethanes, rubbers of low molecular weight, polyethers, polyethylene glycols, etc., showed that a varies from 0.5 to 1 depending on the nature of the solvent, as with high polymers. But several other investigations[50–52] revealed a tendency for a to increase—not to decrease—as the molecular weight fell. Hydrodynamic theories of polymer solutions suggest that, for permeable Gaussian chains[53], such behaviour is probably due to an increase in the permeability of the coils with decreased molecular weight of the polymer. As a consequence, the slope of the plot of $\lg[\eta]$ against $\lg M$ should increase with fall in molecular weight. The Debye–Bueche[54], Kirkwood–Riseman[55,56], and Zimm–Kuhn[57-60] theories predict, with increase in permeability (weakening of hydrodynamic interaction) and short chains, direct proportionality between viscosity and molecular weight ($[\eta] = KM^a$, where $a = 1$), and decrease in the shielding coefficient σ.

Long-range effects (non-ideality of solutions), like short-range effects (chain rigidity), influence the conformations of flexible chains[61,62]. High values of the exponent a obtained in a θ solvent (in the absence of the excluded-volume effect) indicate a loose structure and permeability of the coil, and hence enhanced rigidity of the chain. Nevertheless, volume effects in non-ideal solvents lead to swelling of the coil and to a corresponding increase in a. In order to determine the true flexibility of a macromolecular chain, therefore, the influence of volume effects should be excluded.

Calculation then becomes useful, since the excluded-volume effect can either be disregarded or estimated. Thus at high degrees of polymerisation 32% of terminal groups occur within a sphere described by the radius of inertia of the macromolecule[27]. Nevertheless, taking into account excluded-volume effects lowers the number of end-groups in this sphere to 18%.[23] Thus the excluded-volume effect leads to the removal of terminal groups from the sphere of tne macromolecule.

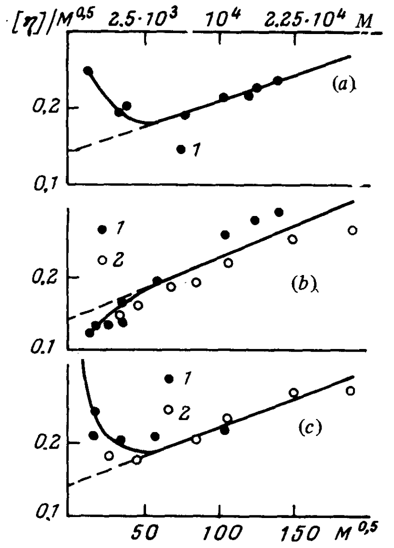

Figure 4. Dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ for polyethylene glycol in: *a*) methanol; *b*) benzene; *c*) water at: 1) 20°C; 2) 30°C.

The theories of Kuhn[58,59], Hearst[63], etc. are applied to rigid chains. With relatively flexible macromolecular chains, which are coiled quite compactly even in good solvents, the flow effect is almost absent, and the Stockmayer–Fixman equation is used[40]. With such molecules volume effects can be eliminated by extrapolating the hydrodynamic parameters to low molecular weights by means of the theory of the excluded volume[48,62]. Stockmayer and Fixman suggested the formula

$$[\eta]=KM^{0.5}+FM,$$

for the molecular-weight dependence of intrinsic viscosity, in which F and K, both independent of molecular weight, represent respectively short-range and long-range interactions. The constants are found by plotting the dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ by means of the Stockmayer–Fixman graph, and thus these interactions are determined for wider molecular-weight limits than is possible from the Mark–Kuhn–Houwink equation.

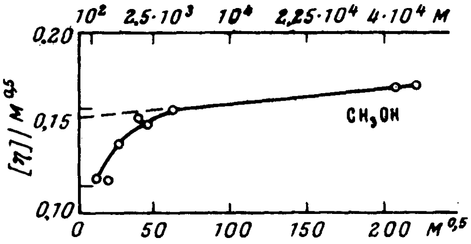

Figure 5. Dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ for the monophenyl ether of polyethylene glycol in methanol at 25°C.

Experimental viscosity results obtained for solutions of polyethylene glycol in methanol, benzene, and water and for its monophenyl ether in methanol[46,64], together with other results[47,48], have revealed more clearly the applicability of the Stockmayer–Fixman equation. Positive and negative departures from the equation are usually observed at a molecular weight of 3000, independent of the nature of the solvent and the end-groups (Figs. 4 and 5). This is apparently due to the effects both of the polymer chain and of the terminal groups. The value of K is independent of the solvent, which indicates that short-range interaction is independent of solvent and end-groups. Positive departures from the equation in methanolic and aqueous solutions of polyethylene glycol are caused by increase in size of the oligomer macromolecules resulting from interaction between terminal hydroxyls and the solvent. Negative deviations, which are observed both in benzene solutions of polyethylene glycol and in methanolic solutions of its monophenyl ether, are apparently caused by coiling of the macromolecule under the influence of repulsive forces between end-groups and solvent molecules. This range of molecular weights is regarded as the region of oligomers, possessing the properties of compounds of low molecular weight.

The general Stockmayer–Fixman equation shows that the intrinsic viscosity of oligomers is proportional to the square root of their molecular weight, which is confirmed by several investigations. Nevertheless, this principle does not hold for certain oligomers: here there is an approximately linear variation with the molecular weight[65]. The Huggins constant K' in the equation

$$\eta_{sp}/c = [\eta] + K'[\eta]^2c$$

is a measure of the affinity between polymer and solvent. On the basis of data for high polymers K' is now regarded as independent of molecular weight[66]. In θ solvents it is usually approximately 0.5 (or greater), and in good solvents $K' = 0.2-0.3$.

However, experiments on oligomers indicate that in most cases the Huggins constant assumes anomalous values. Several studies showed that the constant increases with decrease in the molecular weight of the oligomers[67-69], and may even exceed those for high polymers[70,71]. In certain cases a considerable increase occurs (to several units) with decrease in the chain length[72]. This is governed by the structure of the macromolecules and the nature of the solvent. The variation of K' with molecular weight is usually less marked in poor than in good solvents. Another study showed[73] that the experimental values correspond to the Huggins equation only within a narrow range of molecular weights. The formula

$$K' = eM^{d_0} + b_0,$$

was proposed, in which d_0 and b_0 were independent of molecular weight.

A complicated dependence of K' on molecular weight has been found in several studies[72]. Values of K' are largest at very low molecular weights. Increase in M to 2000–3000 is accompanied by a rapid fall in K', and further increase by a smooth decrease, which then slows down (Fig. 6). The increase in K' with decrease in molecular weight is attributed by some authors to an increase in the density of the coiled macromolecule. Molecules of greater chain length are regarded as more prolate and less spherical than those with short chains. This is apparently because short molecules are densely packed, weakly solvated coils, relatively impermeable to the solvent. This is consistent with diffusion results.

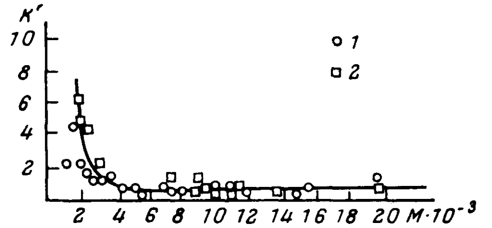

Figure 6. Dependence of the Huggins constant K' on the molecular weight of poly(methyl acrylate) in: 1) acetone; 2) θ solvent.

Dimensions of macromolecular coils approaching the unperturbed values were determined[72-76] from the measured diffusion coefficients of polystyrene in solutions, which enables the Flory coefficient[30] to be calculated. The chain rigidity thus found for the oligomer macromolecule approached that of high polymers, which was attributed to an increased effect of thickness on the chain dimensions[77]. Other workers[78,79] also obtained for certain oligomers (polyoxypropylene and polyoxyethylene glycols) values of q in the equation $D = K_\alpha M^{-q}$ closely similar to the corresponding values for long chains. This indicates that the hydrodynamic characteristics of oligomer molecules in solution can be described quite accurately by hydrodynamic theories based on the model of an impermeable Gaussian coil exhibiting slight thermodynamic interaction with the solvent.

(*b*) Conformational Transitions in Macromolecules of Oligomers

The second virial coefficient A_2 represents the interaction between polymer and solvent:

$$\pi/c = RT\,(1/M + A_2c + \ldots),$$

where R is the universal gas constant, T the absolute temperature, c the concentration, M the molecular weight, and π the osmotic pressure. According to Flory's theory[80,81] A_2 is independent of the molecular weight of the polymer. In practice, however, agreement with theory is found only at the θ point or with slight departures from ideality. The greater the deviation from θ conditions, the more marked is the dependence of the second virial coefficient on the molecular weight.

An equation for this dependence based on many experimental results was[82]

$$A_2 = a_1/M^{0,5} + b_1,$$

where a_1 and b_1 were theoretical constants independent of the molecular weight. Research showed that the equation was valid for exothermic and endothermic systems, as well as for θ conditions over a wide range of molecular weights. In the study of solutions of polystyrene in benzene, toluene, and naphthalene (exothermic systems), for example, a linear dependence was observed for molecular weights from 500 to 5×10^6 (Fig. 7).[14] The corresponding range for an endothermic system (poly(methyl methacrylate) in acetone) was from 200 to 7.8×10^6.[83]

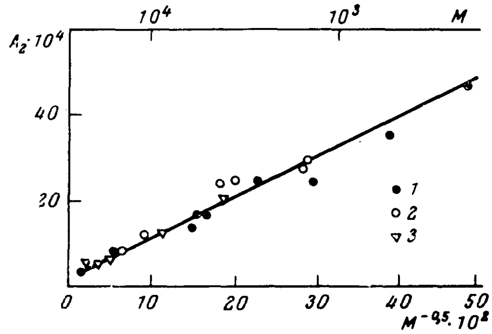

Figure 7. Dependence of second virial coefficient A_2 on molecular weight M for the exothermic systems comprising polystyrene in: 1) naphthalene; 2) benzene; 3) toluene.

Nevertheless, polystyrene[84] and poly(methyl methacrylate)[85] in good solvents showed departures from the suggested equation at low degrees of polymerisation (Fig. 8). In particular, the second virial coefficient was found[84] to be negative for dimers, to reach a positive maximum when $P = 4$, and then gradually to decrease with increase in molecular weight (Fig. 9). These results indicate that the equation holds up to the maximum, where the substance possesses polymeric properties. The presence of a maximum indicates a transition in the form of the macromolecule from coiled to rod-shaped, which can apparently be interpreted as a transition to compounds possessing the properties of polymers.

The above considerations are consistent with the dependence of the entropy contribution B_S on the degree of polymerisation P in the polystyrene–benzene system (Fig. 10).[14] The entropy is approximately zero for the dimer, reaches a maximum when $P = 4$, and then gradually diminishes with increase in molecular weight. It is known to have its maximum value when the molecule is elongated into a rod, and its minimum value when the molecule is coiled into a sphere. Maximum entropy was therefore interpreted as the transition point between extended and coiled states of the molecules.

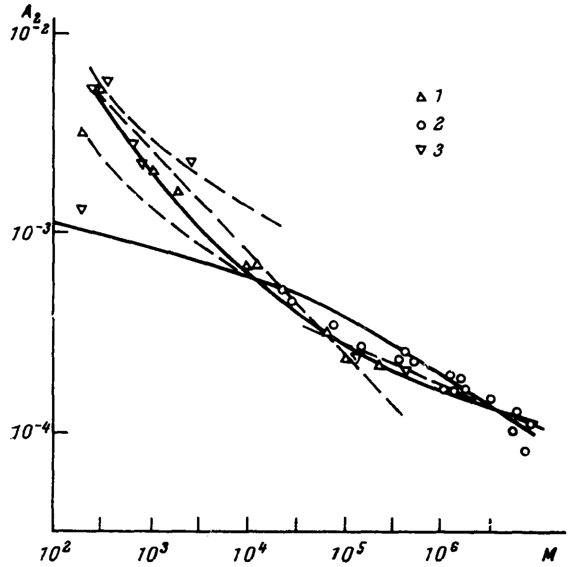

Figure 8. Dependence of second virial coefficient A_2 on molecular weight M for the endothermic system comprising poly(methyl methacrylate) in acetone, obtained by: 1) osmometry; 2) light scattering; 3) X-ray examination.

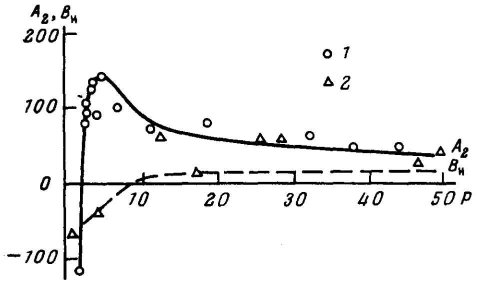

Figure 9. Dependence of second virial coefficient A_2 and of enthalpy coefficient B_H on degree of polymerisation of oligostyrene in: 1) naphthalene; 2) benzene.

Application of a calorimetric method[86] to polystyrene in benzene and cyclohexane, poly(methyl methacrylate) in acetone, and polyvinylcarbazole in benzene showed[84] that, at the initial degrees of polymerisation, the enthalpies of mixing almost always pass through maxima (as do the second virial coefficient and the entropy). Further increase in molecular weight produces hardly any change in the enthalpy (Fig. 11). This effect was explained in terms of the interaction energy of end-groups in the oligomer macromolecules.

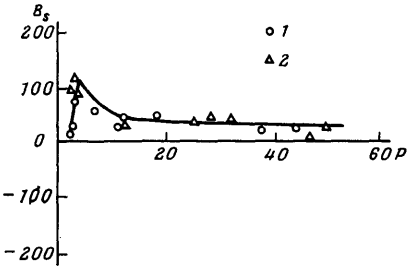

Figure 10. Dependence of entropy coefficient B_S on degree of polymerisation P for oligostyrene in: 1) naphthalene; 2) benzene.

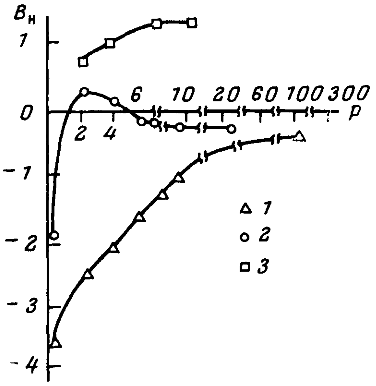

Figure 11. Dependence of enthalpy coefficient B_H on degree of polymerisation for: 1) poly(methyl methacrylate) in acetone; 2) polyvinylcarbazole in benzene; 3) a polycarbonate in dioxan.

(c) Structure Formation in Solution with Increase in Concentration of Low Polymers

With increase in the concentration of dilute solutions of polymers the macromolecules interact and form association complexes or aggregates. Staudinger[87] first formulated the concept of the lowest concentration—the critical concentration c_{cr}—at which the polymer molecules begin to come into mutual contact. Many studies have shown that this concentration depends on the molecular weight of the polymer and its chemical structure, the nature of the solvent, and the temperature. The critical concentration usually increases with decrease in molecular weight, deterioration in the quality of the solvent, and rise in temperature, which is a consequence of the weakening of interaction between the macromolecules under these conditions. It can be determined from the break in the linear concentration dependence of viscosity, intensity of light scattering, optical density, and other properties of the polymer. However, some studies[77,88] of the concentration c dependence of the reduced viscosity η_{sp}/c revealed a breakdown of the linear dependence at subcritical concentrations. These anomalies were attributed to supercoiling of the macromolecules at high dilutions[77,88], and by other workers to decrease in the effective radius of the capillary resulting from adsorption of the polymer on its walls[89,90].

Association begins sooner in oligomers than in high polymers. Incipient structure formation was observed, in solutions of butadiene–acrylonitrile rubbers having molecular weights of $(1.4-2.7) \times 10^4$, at concentrations of 0.1–0.5 g/100 ml.[31] Critical concentrations in benzene solutions of polystyrene of molecular weight $(1.5-33) \times 10^3$ varied from 0.5 to 1.5 g/100 ml.[90]

In several studies[15,91] anomalies were absent up to fairly high concentrations of low polymers in solution. This applied to poly(methyl methacrylate) and poly(ethyl acrylate) of molecular weight $(1-20) \times 10^3$ up to 0.2 g/100 ml.[15] Investigation of dilute solutions ($c < 0.1$ g/100 ml) of SKN-18 [butadiene–acrylonitrile synthetic rubber] at 20–60°C showed that the intensity of light scattering by the solutions remained unchanged with rise in temperature, which indicated that association had not occurred[31]. In solutions containing macromolecules of high polymers at corresponding concentrations, however, the apparent molecular weight decreased at 60°C; this was attributed to the breakdown of association complexes[92].

IV. RHEOLOGICAL PROPERTIES

Considerably less study has been made of the structure of low polymers and their concentrated solutions than of dilute solutions. Only comparatively recently have publications appeared on the rheological properties of certain polyethers and polyisobutylenes of low molecular weight and on those of their solutions. The structural features of polymers and their solutions (great size of macromolecules, formation of network structures, etc.) are responsible for several flow anomalies, e.g. departure from Newton's viscosity law[29]. This is apparent in the rubberlike elasticity possessed by solutions of several polymers.

Unlike high polymers, oligomers possess almost the same capacity for rubberlike elastic deformations, which are in the nature of relaxation processes involving change in the conformations of the macromolecules under the influence of shear stresses. This feature is attributed to great flexibility of the macromolecules and the presence of a mobile, fluctuating network with temporary contacts produced by intermolecular interaction. The systems are mainly thixotropic in character, with relatively unstable bonds and long relaxation times. They can be regarded as a new type of cross-linked systems, occupying a position intermediate between concentrated solutions, polymer jellies, and solutions of substances of low molecular weight capable of cross-linking[6,93,94].

Many methods have now established that several concentration ranges exist in solutions of polymers, differing in degree of order of the chains, conformational properties of the macromolecules, and their interaction. This is responsible for differences in rheological properties[95,96]. The concentration ranges can be arbitrarily divided as indicated below.

1. Very dilute solutions, in which macromolecules are present as isolated coiled coils. With increase in concentration the chain molecules straighten out, interact, and form structures.
2. More concentrated solutions, in which, as a consequence of intermolecular contacts, the macromolecules in the form of prolate coils form the ideal three-dimensional network described by Büche[97] or are arranged in isolated association complexes or aggregates. A structural network appears at higher concentrations of oligomers than of high polymers.
3. Concentrated solutions, in which the ideal network may be consolidated by the formation of new bonds with other macromolecules ($c > c_{cr}$). The macromolecules then have small free volumes and are characterised by considerable mutual penetration of segments.
4. Highly concentrated solutions, in which ordered structures are formed, different for polymers in different physical states and of different chain lengths[98]. The mutual interlacing of segments of the macromolecules produces a continuous network of bonds, with a consequent considerable increase in viscosity[97].

All the above ranges for transformation in polymer solutions are reversible with change in concentration. Examination of the viscoelastic properties of such solutions over all concentration ranges will give an idea of the nature and the rates of redistribution of conformations of chain molecules, as well as of their mutual arrangement, i.e. of the structure of the solutions[99,100].

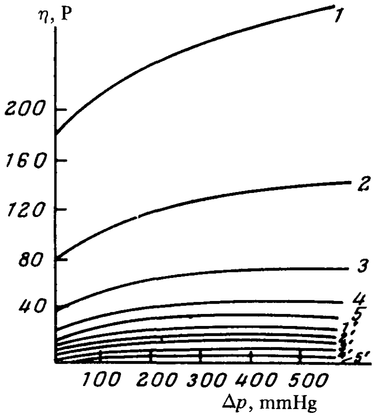

Figure 12. Flow curves for polyesters—poly(ethylene glycol adipates)—of molecular weight 2050 and 790 (unprimed and primed curves respectively) at (°C): 1) 20; 2) 30; 3) 40; 4) 50; 5) 60.

Study of the flow of certain oligomers and their concentrated solutions has shown a difference in rheological behaviour between these compounds and high polymers. For example, investigation of polyethers—polyoxolanyloxypropylene glycols—and polyesters—poly(diethylene glycol adipates)—and their concentrated solutions has shown[101] that the viscosity of the system in a longitudinal velocity gradient (in a capillary viscometer) increases with the shear stress, in some cases reaching a maximum. These antithixotropic effects degenerate with rise in temperature and with dilution. They were attributed to intensified interaction of the macromolecular chains of the oligomers on orientation in the flow. The viscosity is then affected by the molecular weight. With several oligomers such antithixotropic effects develop only at low stresses. When the shear stress arises above a critical value, thixotropic breakdown of the previously formed structure occurs, and the usual process of flow is observed, as with high polymers[102]. Other studies[103-105], using both capillary and rotary viscometers, revealed in the oligomers investigated and their concentrated solutions, together with thixotropic breakdown, a region of antithixotropy at low shear stresses. This phenomenon is also connected with intensified interaction of oriented macromolecules under the influence of transverse and longitudinal velocity gradients. Anomalous viscosity effects are more marked with oligomers of lower molecular weight, which can be explained by the enhanced rigidity of shorter chains and their greater mobility (Fig.12).

Büche[106] used the concept of free volume to develop theoretically the resistance to the flow of polymers, which arises from interaction between segments, mutual friction of segments during movement of the polymer chain, and the formation of a network structure by the meshing of segments and macromolecular chains. Relative movement of macromolecules is facilitated with decrease in the molecular weight of the polymer or dilution of its solution, and flow becomes more intense. This is apparent in a decrease in viscosity and in the heat of activation of viscous flow[107,108], which, after certain fairly high degrees of polymerisation have been reached, remains constant and independent of molecular weight[103]. The smaller the macromolecules the higher the concentrations at which intermolecular interaction and departure from Newtonian flow become apparent.

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Enzyme Electrodes

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The literature data on the use of immobilised enzymes in analytical chemistry are reviewed and the fundamental conditions for the creation of kinetic methods in enzymatic analysis are described. The types of enzyme electrodes and the factors influencing the response of such electrodes, their stability, and sensitivity are discussed in detail. The possible pathways towards further development of enzyme electrodes for use in laboratory and technological practice and for monitoring the environment are considered.

The bibliography includes 69 references.

CONTENTS

I. INTRODUCTION

The last decade has been marked by a vigorous development of research in the field of the immobilisation of enzymes and their use for technological, analytical, and scientific purposes. The conversion of enzymes into a water-insoluble state with retention of catalytic activity made it possible to extend greatly our ideas concerning the possibility of using bio-organic catalysts in a wide variety of different fields of chemistry, fine chemical engineering, pharmacology, and medicine. Because of their high specificity, enzymes have already been used for many years in analytical chemistry; hundreds of studies devoted to kinetic methods in enzymatic analysis are published annually. The use of immobilised enzymes for these purposes stimulated the creation of methods of "reagent-free" analysis whereby continuous analysis of aqueous solutions of organic (and in many instances inorganic) compounds is possible in principle.

In their turn, the achievements in this field have promoted the development of effective methods for monitoring the state of the environment, clinical diagnosis, etc. Finally, the so called "enzyme electrodes", developed in recent years, permit rapid automatic analysis of multicomponent systems on the basis of combined "electrode-enzyme" electrochemical systems which exhibit a high selectivity in the determination of individual compounds or classes of compounds.

The attention devoted at the present time to the development of enzyme electrodes and to the study of the prospects for their application in analytical chemistry is partly due to the vigorous development of methods for the isolation, purification, and identification of enzymes. According to data presented at the Symposium on Biotechnology and Bioengineering in Henicker[1], the number of enzymes which have been discovered and characterised has increased from 80 in 1928 to 1500 in 1969, and continues to grow exponentially with a ten-year doubling period.

The present review is an attempt to summarise and give a systematic account of studies on the use of immobilised enzymes in analytical chemistry published up to April 1974, and to assess the immediate prospects in this field.

II. THE SPECIFICITY OF ENZYME ACTION

The most characteristic feature of enzymatic catalysis is the specificity of enzyme action. At least three general qualitative types of specificity have now come to be differentiated from this extremely comprehensive term: specificity with respect to the medium, specificity with respect to the reaction, and substrate specificity (specificity with respect to the structure of the substrate). The first two types of specificity are usually expressed in the fact that the enzyme catalyses a reaction of a particular type under specified conditions and constitutes the basis for the subdivision of enzymes into the corresponding classes (oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases or synthetases)[2]. The substrate specificity of the enzyme is its most characteristic feature, which has not yet found adequate analogies in non-enzymatic catalysis, and makes it possible to characterise unambiguously and to identify the given enzyme among hundreds and thousands of others. The usual phenomenon in enzymatic reactions is that the enzyme catalyses the reaction of only one stereochemical form of the substrate, being completely inactive in relation to other stereoisomers (the so called stereochemical specificity of the enzyme).

In many instances the enzyme exhibits absolute specificity, catalysing the reaction of only one substance and not reacting with its derivatives or homologues. Thus, butanediol dehydrogenase catalyses the conversion of butane-2,3-diol into acetoin, but altogether fails to oxidise ethylene glycol, glycerol, ethanol, isopropyl alcohol, isobutyl alcohol, isopentyl alcohol, or glucose[3]. Lactaldehyde reductase, which catalyses the reversible conversion of D-lactaldehyde into propane-1,2-diol, is completely inactive in relation to L-lactaldehyde, acetaldehyde, propionaldehyde, glycolaldehyde, acetol, glyoxylic acid, pyruvic acid, D-galactose, D-mannose, D-fructose, D-or L-arabinose, and L-rhamnose[4]. Mannitol dehydrogenase, which catalyses the conversion of D-fructose into mannitol, does not act on D-glucose, D-mannose, or D-ribose[5]. The activity of glucose oxidase, which oxidises β-D-glucose with formation of gluconic acid, is four times lower with respect to 2-deoxy-D-glucose, 50 times lower with respect to 6-methyl-D-glucose, 100 times lower with respect to D-mannose and D-xylose, and 200 lower with respect to α-D-glucose; the enzyme altogether failed to have any action on the remaining 80 sugars which had been tested as substrates[6]. Formaldehyde dehydrogenase, which oxidises formaldehyde to formic acid, does not react with acetaldehyde, glycolaldehyde, and benzaldehyde[7]. Benzaldehyde dehydrogenase, which converts benzaldehyde into benzoic acid, altogether fails to oxidise acetaldehyde, propionaldehyde, crotonaldehyde, formaldehyde, and DL-glyceraldehyde[8]. Among all the aliphatic aldehydes, aminobutyraldehyde dehydrogenase acts only on 4-aminobutyraldehyde, oxidising it to 4-aminobutyric acid[9].

On the other hand, many enzymes exhibit broad specificity without the imposition of stringent requirements on the structure of the substrate. Thus a large number of compounds having the general formula $R_1CH(R_2)COR_3$, where the substituents R_1, R_2, and R_3 can have virtually infinitely variable structures, can serve as substrates for α-chymotrypsin[10]. The extremely broad specificity of α-chymotrypsin may be illustrated by the fact that this enzyme is capable of catalysing the hydrolysis of proteins, peptides, esters, amides, hydrazides, alkylamides, acid anhydrides, acid chlorides, hydroxamides, anilides, thioesters, oxazolones, cyclic peptides, cyclic phosphates, lactones, and sultones; in some cases it is also capable of cleaving the C–C bond. Aldehyde oxidase exhibits group specificity with respect to aliphatic aldehydes, catalysing the oxidation of formaldehyde (1.0), acetaldehyde (4.6), propionaldehyde (5.1), butyraldehyde (12.2), valeraldehyde (2.4), and crotonaldehyde (7.6); the relative reactivities of the aldehydes in this enzymatic reaction are indicated in brackets[11].

The high enzyme specificity (absolute or group specificity) in combination with favourable factors such as the high rate of enzymatic processes, the mild reaction conditions (room temperature, atmospheric pressure, neutral pH of the medium, etc.), and a fairly wide selection of available enzymes have ensured the development of a new trend in analytical chemistry—kinetic methods in enzymatic analysis. Enzyme-catalysed reactions are used to determine substrates, inhibitors, activators, and in many instances the enzymes themselves (this applies primarily to the analysis of biological liquids in clinical laboratories). The use of enzymes in analytical chemistry has been considered in a number of reviews and monographs[12-19]. However, despite a number of the evident advantages of kinetic methods in enzymatic analysis, their use in laboratory practice has so far been fairly limited. One of the main reasons for this is still the high cost of the majority of enzymes, which virtually precludes the large-scale application of enzymatic analytical methods (because enzymes can be used only once owing to the extremely laborious procedures needed for their regeneration from the mixture). This disadvantage is compounded also by the low stability of the majority of enzymes, which frequently leads to their complete inactivation in several days, and sometimes in several hours under the optimal conditions for analytical purposes.

Thus, in order to increase the "technological applicability" of enzymes, it is necessary to increase their stability, on the one hand, and to ensure the possibility of their repeated use on the other. In principle this is achieved by converting enzymes into heterogeneous catalysts by immobilising them.

III. THE IMMOBILISATION OF ENZYMES

The immobilisation of enzymes is a procedure whereby they are converted into a water-insoluble state with retention (partial or complete) of catalytic activity. Immobilised enzymes are usually obtained by the following methods (see the relevant reviews[20-24]):

1. The covalent attachment of enzyme molecules to a water-insoluble carrier (cellulose, agar, dextran, glass, paper, fabrics, polystyrene, nylon, metals, ion-exchange resins, etc).
2. The entrainment of the enzyme in a gel or polymer network.
3. The covalent cross-linking of enzyme molecules with one another using a di- or poly-functional reagent.
4. The adsorption of the enzyme on water-insoluble carriers (as a rule ion-exchange resins).
5. Microencapsulation (the enclosure of an enzyme solution in semipermeable capsules 5–300 μm in size).

The first two immobilisation methods are most often used. The covalent binding of the enzyme to a carrier leads to a stable system in which the protein cannot be desorbed when the temperature, pH, or the ionic strength of the reaction medium are changed, and also when the substrate is added to the reaction medium. The method based on the entrainment of the enzyme in a gel is distinguished by simplicity and the absence of appreciable influences on the active centre of the enzyme. In any case the immobilisation of enzymes makes possible their repeated use in practice when catalytic processes are carried out in periodic or continuous operation "enzyme reactors". Furthermore, the immobilisation of enzymes frequently increases their stability. According to the data quoted in Melrose's review[21], in thirty out of fifty different variants of immobilisation the stability of the immobilised enzyme was higher than that of the corresponding soluble enzymes, in eight cases the stability decreased on immobilisation, and in twelve cases the stability hardly changed following immobilisation.

Bearing in mind that the stability of immobilised enzymes is influenced to a high extent by the nature of the carrier, the nature of the grafting agent, and the method and conditions of the immobilisation (in all instances there is a possibility of a large number of different variants), it is clear that the possibilities of stabilising enzymes on immobilisation have been by no means exhausted. As an example, one may quote the data of Kaplan and coworkers[25] according to which lactate dehydrogenase, which loses 100% of its activity after incubation for approximately 1 h, retains its activity fully under the same conditions for at least 35 days following immobilisation on porous glass with the aid of glutaraldehyde.

IV. THE APPLICATIONS OF IMMOBILISED ENZYMES IN ANALYTICAL CHEMISTRY

The use of immobilised enzymes, whereby routine chemical analyses can be carried out on individual samples or in a stream (with repeated employment of the same enzyme preparation), has to a large extent solved the problem of the high cost of enzymatic analytical methods and has frequently increased the accuracy of the analytical procedure. There exist two general approaches to the analytical determination of the concentrations of reagents (substrates) in the test system. In one of them the enzymatic reaction is continued until the complete exhaustion of the substance to be determined (or until the attainment of an equilibrium in the system between the initial reactants and products), while recording at the same time the change in a suitable physical or chemical property of the system, the amount of substrate in the initial specimen being calculated from the amount of product formed. In the second approach use is made of kinetic analytical methods, the rate of appearance of the product or of the disappearance of the substrate in the enzymatic reaction being determined and the initial substrate concentration being calculated from the corresponding calibration curve. This method is also applicable to the determination of the concentrations of effectors (inhibitors or activators), which are present in the reaction system. Both approaches have been applied in practice using immobilised enzymes.

The first study in which the use of immobilised enzymes for analytical purposes was described was carried out in 1965 by Guilbault and coworkers [26], who found that cholinesterase entrained in a starch gel and deposited on a foam plastic plate (to increase the mechanical strength of the immobilised enzyme) retained its activity for 12 h. The activity of the enzyme in the hydrolysis of butyrylthiocholine iodide was determined electrochemically using platinum electrodes between which a direct current was passed. Depending on the rate of the enzymatic reaction, the potential of the system changed from 150 mV (the oxidation potential of the reaction product–thiocholine) to 350–400 mV (the potential of the oxidation of the iodide of the substrate to iodine), which made it possible to investigate the influence of the added effectors on cholinesterase under continuous conditions. In the same year Guilbault and Kramer [27] used similarly immobilised cholinesterase to detect small amounts of organophosphorus insecticides in air. Foam plastic plates impregnated with starch gel containing immobilised cholinesterase have been used recently to devise a continuous analyser for water designed to detect rapidly subtoxic concentrations of anticholinesterase compounds [28].

A common disadvantage of all these devices is their instability due to the appreciable elution of the enzyme from the starch gel. Coprecipitation of cholinesterase with aluminium hydroxide and suspension of the resulting preparation in a starch gel with subsequent impregnation of a foam plastic plate enabled Goodson et al. [29] to obtain a stable enzyme system capable of functioning for 56 h without appreciable loss of enzyme. During this period, 2700 litres of water were passed through the carrier with the immobilised cholinesterase. According to the results of Goodson et al. [29], the immobilised enzyme gives a response after 3 min when water contains 0.2 part per million of 2,2-dichlorovinyl dimethyl phosphate. Gutknecht and Guilbault [30] also reported the development of an enzyme system for the continuous monitoring of cyanide ions in drainage waters, which is based on the specific reaction of immobilised injectase (β-cyanoalanine synthase).

Hicks and Updike [31] determined glucose and lactic acid by means of a column with glucose oxidase and lactase dehydrogenase immobilised on a polyacrylamide gel. The substrate specimens were passed through columns filled with gel-enzyme particles of standard size and subjected to lyophilic drying, mixed with indicators changing colour on interaction with the corresponding products of enzymatic reactions, and passed through the spectrophotometer cuvette. The authors [31] noted an appreciable increase of the stability of lactase dehydrogenase following immobilisation in the gel. Thus at 37°C the activity of soluble lactase dehydrogenase decreases to 10% of the initial value after 2 h, while that of the gel-enzyme remains completely unchanged for 10 h under the same conditions. Guilbault and Das [32] made a comparative study of starch and polyacrylamide gels as carriers for the immobilisation of cholinesterase and urease. Noting that immobilisation in the starch gel can be carried out under milder conditions, the authors [32] point out the higher stability of enzymes in the polyacrylamide gel.

Hornby et al. [33] developed a method for the automated analysis of solutions for glucose having immobilised glucose oxidase on the inner surface of a polystyrene tube (375 cm long, with an internal diameter of 2 mm). The activity of the enzyme was recorded at 35°C and pH 5.6 by the calorimetric determination of hydrogen peroxide (the product of the enzymatic reaction) using potassium iodide. The apparatus permitted 40 analyses per hour, glucose being determined quantitatively over the concentration range 5×10^{-4} M–10^{-2} M. According to the authors' data [33], the tube with immobilised glucose oxidase did not exhibit an appreciable loss of catalytic activity in the course of 1.5 months.

Subsequently Hornby and coworkers abandoned the polystyrene carrier because of its pronounced hydrophobic properties, and their later studies on the immobilisation of enzymes [34–36] were carried out using nylon. Thus urease, bound via glutaraldehyde to the inner surface of a partly hydrolysed nylon tube [34,35] (2 m long, with an internal diameter of 1 mm), was used to determine urea in the course of four months, more than 400 analyses being carried out during this period. Urate oxidase, immobilised on a nylon powder, was used to analyse aqueous solutions of uric acid [35] in the concentration range 10^{-5}–10^{-4} M. However, carboxy-groups, ionised under experimental conditions, remain on the carrier surface after partial hydrolysis of the nylon, which makes the carrier unsuitable for the immobilisation of many enzymes.

In order to extend the scope of the proposed method, Hornby et al. [36] converted the carboxy-group of the carrier into an amide form by treatment with *NN*-dimethyl-1,3-propylenediamine and used the modified carrier to immobilise lactate dehydrogenase, malate dehydrogenase, and alcohol dehydrogenase, which permitted the analysis of aqueous solutions for pyruvic acid, oxaloacetic acid, and ethanol respectively. According to their data [36], the method is suitable for the quantitative determination of 4×10^{-5}–2×10^{-4} M pyruvate, 2×10^{-5}–1.6×10^{-4} M oxaloacetate, and 0.01–0.1 M ethanol. All the immobilised enzymes fully retained their activity in the course of 20 days. During this period, each was used to perform at least 1000 analyses. Under these conditions, the soluble enzymes lost more than 90% of their activity.

In a recent study by Weibel et al. [37], a general method was developed, in relation to the analysis of solutions for their glucose content, for quantitative determination of compounds in the course of the enzymatic conversion of which oxygen dissolved in water is absorbed. In the determination of glucose, the solution analysed is passed with the aid of a micropump through a 5 × 35 mm column containing glucose oxidase bound covalently to porous glass and is passed through a cell containing a Clark oxygen electrode. The analysis can be carried out either under kinetic conditions or on the basis of the degree of reaction established following the completion of the enzymatic process. A single analysis takes 2 min and the error in the determination of glucose does not exceed 1–2%. According to the results[37], the column functions for more than 2 weeks when used daily in the course of 8 h.

Mosbach and coworkers[38] described the use of flow microcalorimetry in kinetic methods for enzymatic analysis using immobilised enzymes. The advantages of the method are the possibility of analysing opaque solutions and high sensitivity (down to 10^{-6} M of the substance to be determined).

An interesting and very promising approach to the selective determination of small amounts of metals was demonstrated recently by Stone and Townshend[39,40]. Fungal polyphenol oxidase was immobilised by being bound covalently to Enzacryl AA (obtained by reducing a copolymer of acrylamide, *p*-nitroacrylanilide, and *NN'*-methylenebisacrylamide) and was then dialysed until the complete removal of copper(II) ions forming part of the enzyme active centre. The resulting inactive apoenzyme is reactivated reproducibly and very selectively on being incubated with trace amounts of Cu^{2+} (10–200 ng), the observed rate of the enzymatic reaction being unambiguously related to the Cu^{2+} concentration in the solution being analysed (a linear relation between the rate of reaction and the concentration of copper ions in solution was observed in the concentration range 10^{-7}–2×10^{-6} M Cu^{2+}). The authors[39] noted that, in relatively large volumes of solutions being analysed, it is possible to determine 10^{-15} mg/ml of Cu^{2+} ions with the aid of this method. The stability of the immobilised polyphenol oxidase makes it possible to store it for 3 months in aqueous solution at pH 7.0 and 6°C.

In all the analytical applications of immobilised enzymes described above, the enzyme activity was determined by the reaction of the biocatalyst with the corresponding substrates or by the reaction of products of the enzymatic reaction with the corresponding indicators specially introduced into the test system. However, "reagent-free" enzymatic analytical methods, based on the use for this purpose of the so called "enzyme electrode" consisting of electrochemical devices on the sensor element of which an immobilised enzyme is deposited, have been developed to the greatest extent at the present time. Such an electrode possesses the fundamental properties required for the analytical system—specificity to the given reaction and the reagent being determined (provided that the latter is a specific substrate of the given enzyme)—and permits rapid analysis of the reaction mixture (generally speaking, the rate of analysis depends both on the characteristics of the electrochemical system itself and on the values of the kinetic parameters of the enzymatic reaction).

When the enzyme electrode comes into contact with the test solution, containing, in particular, the specific substrate of the given enzyme, the enzymatic reaction takes place in the layer near the electrode. If the product (or the substrate) of the reaction is electrochemically active, then the rate of the absolute change in electrode potential is a measure of the amount of the reagent being determined in the mixture subjected to analysis. The advantage of this analytical method is that it can be automated and continuous quantitative determination of the given reagents, including those in complex chemical or physiological systems, is possible.

The first enzyme electrode, constructed for a continuous determination of the concentration of glucose with the aid of immobilised glucose oxidase, was described by Updike and Hicks[41] in 1967. The same authors introduced the term "enzyme electrode"[41,42] for a system consisting of the polarographic oxygen electrode on the surface of which a layer of polyacrylamide gel 25–50 μm thick with entrained glucose oxidase has been deposited. When the electrode prepared in this way is immersed in a solution containing glucose, the substrate and oxygen diffuse from the solution into the layer of the gel-enzyme. The enzymatic oxidation of glucose

$$\beta\text{-D-glucose} + O_2 \rightarrow \text{D-glucono-}\delta\text{-lactone} + H_2O_2, \qquad (1)$$

which takes place in the immediate vicinity of the electrode surface, reduces the diffusional flux of oxygen through the plastic membrane of the Clark oxygen electrode, which in turn leads to an increase of the electrode current. Thus the change of the current in the electrode system depends on the rate of the enzymatic reaction and hence on the concentration of glucose in the mixture being analysed. By plotting the appropriate calibration curve, the authors[41–43] were able to determine glucose quantitatively also in biological solutions and tissues.

A similar principle served as a basis of the design of other enzyme electrodes (see the next Section), the characteristics of which are compiled in Table. Each electrode is specific either to one particular compound (urea, L-asparagine, L-glutamine, D-glucose, etc.) or exhibits group specificity (L- or D-aminoacids, primary alcohols, various penicillins). Naturally, the nature of the selectivity of the enzymatic reaction determines the region where the given enzyme electrode can be applied.

The use of coupled enzymatic reactions for analytical purposes leads to fundamentally new possibilities in the preparation of selective enzyme electrodes. This approach has so far been demonstrated only on a single example—the determination of L-phenylalanine with the aid of L-aminoacid oxidase and peroxidase, immobilised in a polyacrylamide gel on the surface of an electrode sensitive to iodide ions[44]. The operation of the electrode in the coupled enzyme system is based on the following reactions:

$$\text{L-aminoacid} + O_2 \xrightarrow{\text{L-aminoacid oxidase}} \text{2-oxo-acid} + NH_3 + H_2O_2; \qquad (2)$$

$$H_2O_2 + 2H^+ + 2I^- \xrightarrow{\text{peroxidase}} I_2 + 2H_2O. \qquad (3)$$

During the enzymatic reaction, the steady-state concentration of iodide ions at the electrode surface decreases, the rate of decrease of the I^- concentration depending on the amount of L-phenylalanine in the solution being analysed[44].

V. THE DESIGN OF ENZYME ELECTRODES

All enzyme electrodes consist of an electrochemical sensor of one type or another, on which a layer of immobilised enzyme is deposited. Apart from the polarographic oxygen electrode, which has been used for the analytical determination of glucose with the aid of immobilised glucose oxidase[41–43], this reaction has also been followed by an enzyme electrode based on a platinum disc coated with a thin layer of glucose oxidase bound chemically to a polyacrylamide gel[45,46]. The electrode is immersed in the solution to be analysed and a potential of 0.6 V is established in the system (with respect to the saturated calomel electrode). Glucose diffuses to the layer of the gel-enzyme on the electrode, where it reacts in accordance with Eqn. (1). The hydrogen peroxide formed is oxidised on the platinum electrode, so that the observed current is proportional to its concentration and hence to the initial concentration of glucose. Wingard et al.[47], who used a different design of the platinum electrode, determined by a similar method the concentration of glucose with the aid of immobilised glucose oxidase. Polarographic enzyme electrodes have also been used by Clark for the analytical determination of glucose[48] and L-aminoacids[49] with the aid of immobilised glucose oxidase and L-aminoacid oxidase. Recently Clark[1] developed a method for the determination of methanol and ethanol in aqueous solutions and vapours with the aid of a polarographic enzyme electrode containing immobilised alcohol dehydrogenase. The sensitivity of the enzyme electrode is such that it gives an appreciable response to human breath 16 h after the consumption of alcoholic drinks.

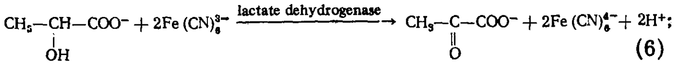
Williams et al.[50] described an enzyme electrode in which glucose oxidase immobilised in a gel was deposited on a platinum electrode and covered by a dialysis film to prevent the diffusion of the enzyme into the solution. The glucose in the solution being analysed diffuses into the layer of gel-enzyme in an amount proportional to its bulk-phase concentration. A distinctive feature of the enzyme electrode employed in this investigation[50] is that benzoquinone was used as the oxidant instead of oxygen. It was shown[50] that benzoquinone can also oxidise glucose under the influence of glucose oxidase, so that the reaction mechanism in the layer near the electrode and on the electrode can be formulated as follows:

$$\text{glucose} + \text{benzoquinone} + H_2O \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + \text{hydroquinone}; \qquad (4)$$

$$\text{hydroquinone} \xrightarrow{Pt} \text{benzoquinone} + 2H^+ + 2e. \qquad (5)$$

The advantage of this method is that the concentration of benzoquinone in the reaction mixture can be readily followed. In addition, there is a possibility of measurements over a longer linear range of glucose concentrations compared with the method in which the oxygen content in the aqueous solution is recorded during the reaction. By carrying out the reaction in a buffer solution (to keep the pH constant during the reaction) and by recording the current in the electrode system, it is possible to determine quantitatively the glucose content in the mixture being analysed.

A similar approach was used by Williams et al.[50] for the analytic determination of lactic acid with the aid of immobilised lactate dehydrogenase:



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}COO^- + 2Fe(CN)_6^{3-} \xrightarrow{\text{lactate dehydrogenase}} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}COO^- + 2Fe(CN)_6^{4-} + 2H^+; \qquad (6)$$

$$2Fe(CN)_6^{4-} \xrightarrow{Pt} 2Fe(CN)_6^{3-} + 2e. \qquad (7)$$

The oxidation of lactate by hexacyanoferrate(III) is catalysed by a preparation of yeast lactate dehydrogenase containing cytochrome B_2 as the cofactor.

Ion-selective electrodes, on the basis of which a major proportion of enzyme electrodes have been constructed, are fundamentally distinctive electrochemical sensors. The first enzyme electrode of this type was proposed in 1969 by Guilbault and Montalvo[51,52] for the quantitative determination of urea in aqueous solutions. It was prepared by depositing a layer of polyacrylamide gel containing urease on the surface of a glass cation electrode sensitive to ammonium ions. When the enzyme electrode is immersed in a solution containing urea, the substrate diffuses into the layer of immobilised enzyme, which catalyses the hydrolysis of urea via the following mechanism:

$$H_2N{-}CO{-}NH_2 + 2H_2O + H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- \ . \qquad (8)$$

Ammonium ions, which are products of the hydrolytic reaction, are recorded by the cation electrode, so that the observed potential is proportional, within certain limits, to the concentration of urea in the sample being analysed.

This approach was subsequently developed by Guilbault and coworkers for the determination of L- and D-aminoacids[53-58], asparagine[55], and glutamine[59]. However, the authors noted[56,57,60] that the selectivity of commercial cation electrodes so far precludes their use for the analysis of biological liquids without a preliminary removal of the interfering K^+ and Na^+ ions by ion exchangers. The modification of enzyme electrodes is therefore directed at the present time mainly towards an improvement of the selectivity of their electrochemical response (see the next Section).

Characteristics of enzyme electrodes.

Enzyme	Method of immobilisation	Substance to be determined	Sensitivity	Response time	Stability	Conditions of determination	Refs.
Urease	entrainment in gel	urea	10^{-3}-1 mg ml^{-1}	25-60 s	–	$[E]_0$ = 175 mg ml^{-1}	51
	entrainment in gel	urea	5 x 10^{-5}-10^{-2} M	40-60 s	2 weeks	$[E]_0$ = 175 mg ml^{-1}, 25°, pH 7.0 (tris-buffer)	52,56,67
	entrainment in gel and enclosure in cellophane film	urea	5 x 10^{-5}-10^{-2} M	–	3 weeks at 25° without appreciable decrease of activity	ditto	52,56,57
	entrainment in gel and enclosure in cellophane film	urea	11-81 mg %	–	–	in blood serum	56
	entrainment in gel and enclosure in cellophane film	urea	0.55-3.50 g/100 ml	–	–	in urine	56
	entrainment in gel	urea	10^{-5}-10^{-2} M	60-180 s	1 week without appreciable loss of activity	$[E]_0$ = 175 mg ml^{-1}, 25°, pH 7.0 (tris buffer)	57
	enclosure between electrode and dialysis film	urea	5 x 10^{-5}-10^{-2} M	–	–	$[E]_0$ = 100 mg ml^{-1}, 25°, 0.1 M NaCl, pH 7.0 (tris buffer)	61
	entrainment in gel	urea	10^{-5}-10^{-3} M	15 min	more than 2 weeks	37°, pH 7.4 (physiological saline soln.)	61

Table (contd.).

Enzyme	Method of immobilisation	Substance to be determined	Sensitivity	Response time	Stability	Conditions of determination	Refs.
L-Amino-acid oxidase	entrainment in gel	L-phenylalanine	10^{-4}–5×10^{-3} M	60–120 s	more than 1 week	$[E]_0 = 200$ mg ml^{-1}, 25°C, pH 7.2	53,54
	enclosure between electrode and cellophane film	L-phenylalanine	–	30–80 s	2 weeks	$[E]_0 = 100$ mg ml^{-1}	56
	enclosure between electrode and cellophane film	L-phenylalanine	10^{-4}–5×10^{-3} M	60–120 s	2 weeks	$[E]_0 = 100$ mg ml^{-1} 25°, pH 7.2–7.5 (tris buffer)	54
		L-leucine	10^{-4}–5×10^{-3} M	–	–	–	54
		L-methionine	10^{-4}–5×10^{-3} M	–	–	–	54
		L-alanine	10^{-3}–5×10^{-3} M	–	–	–	54
		L-proline	10^{-3}–5×10^{-3} M	–	–	–	54
	chemical binding to gel (azo-coupling with polymer of o-aminoanilide of acrylic acid)	L-phenylalanine	10^{-4}–10^{-2} M	60–180 s	–	25°	58
L-Aminoacid oxidase–peroxidase	ditto	L-phenylalanine	5×10^{-5}–10^{-3} M	less than 30 s	decrease of activity by 4–5% after 3 weeks	25°, pH 5.0 $[KI] = 5\times10^{-5}$ M	58
		L-leucine	3×10^{-4}–10^{-3} M	–	–	–	
		L-methionine	3×10^{-3}–10^{-3} M (2% reproducibility)	–	–	–	
D-Aminoacid oxidase	entrainment in gel	D-phenylalanine	–	–	–	–	
		D-alanine	–	–	–	–	
		D-valine, D-methionine, D-leucine, D-norleucine, D-isoleucine	5×10^{-5}–10^{-2} M	–	3 weeks without appreciable loss of activity	25°, pH 8.2 (tris buffer)	55
	enclosure between electrode and dialysis film	–	–	–	appreciably less stable than previous electrode	–	55
Penicillinase	entrainment in gel	benzylpenicillin, ampicillin, nafcillin, phenoxymethylpenicillin, cyclicillin, dicloxacillin	10^{-4}–5×10^{-2} M (reproducibility varied from 9 to 17% in 3 days for different electrodes)	15–30 s	2 weeks (after this the time required for readings increases by a factor of 3–5)	$[E]_0 = 125$ mg ml^{-1}, pH 6.4. room temp., (not measured)	62
	enclosure between electrode and dialysis film	benzylpenicillin	5×10^{-4}–10^{-2} M	2 min	3 weeks	$[E]_0 = 50$ mg ml^{-1}, pH 6.8 (phosphate buffer), 0.1 M NaCl	61
Asparaginase	entrainment in gel	L-asparagine	5×10^{-6}–10^{-2} M	–	28 days without appreciable loss of activity	$[E]_0 = 25$ units ml^{-1}, 25°, pH 8.0 (tris buffer)	55
	enclosure between electrode and dialysis film	L-asparagine	–	–	50% loss of activity after 4 days	ditto	55
Glutaminase	entrainment in gel*	–	–	–	–	–	59
	enclosure between electrode and dialysis film	L-glutamine	10^{-4}–10^{-1} M	1–2 min	12 h	$[E]_0 = 150$ mg ml^{-1}, 25°, pH 5.5 (tris buffer)	59
β-Glucosidase	entrainment in gel	amygdalin	10^{-5}–10^{-2} M	15–40 s	3 days	$[E]_0 = 100$ mg ml^{-1}, 25°, pH 10.4	64
	entrainment in gel and enclosure in cellophane film	amygdalin	5×10^{-6}–10^{-3} M	1 min	crystalline membrane dissolves after 200 hours of continuous operation	$[E]_0 = 50$ mg ml^{-1}, 25°, pH 12.7	63
Glucose oxidase	entrainment in gel	glucose	–	–	–	37°, pH 3.2–10.3	47
	entrainment in gel	glucose	0.15–2.0 mg ml^{-1}	30–180 s	± 10% change in activity after the first 24 h at room temp.	$[E]_0 = 1$ mg ml^{-1} or 10 mg ml^{-1}, pH 7.4 (phosphate buffer)	41
	enclosure between electrode and dialysis film	glucose	10^{-3}–10^{-1} M	–	–	$[E]_0 = 200$ mg ml^{-1}, pH 6.9 (phosphate buffer), 0.1 M Na_2SO_4	61
	enclosure between electrode and dialysis film	glucose	2×10^{-3}–2×10^{-2} M	3–10 min	–	pH 4 (phosphate buffer) or blood; $[E]_0 = 1$ mg ml^{-1}	50
	chemical binding to gel	glucose	5×10^{-4}–2×10^{-2} M	12 s (from init. velocities or 1 min steady-state current)	increase of activity at a rate of 1.4% in 20 days followed by a decrease at a rate of 0.3–0.7% per day for 300 days	pH 6.0 or 6.6 (phosphate buffer), 30°	45,46
	entrainment in gel	glucose	5×10^{-4}–2×10^{-2} M	ditto	increase of activity from 0 to maximum in 40 days followed by a decrease at a rate of 0.3–0.4% per day for 160 days	pH 6.6 (phosphate buffer), 30°	46

Table (contd.).

Enzyme	Method of immobilisation	Substance to be determined	Sensitivity	Response time	Stability	Conditions of determination	Refs.
	entrainment in copolymer of ethylene glycol methacrylate and ethylene glycol dimethacrylate (in proportions of 100:1)	glucose	–	1 min	1.5% decrease of activity per day at 25°C	$[E]_0$ = 1-10 mg ml^{-1}, pH 7.2 (phosphate buffer), 25°	69
	enclosure between electrode and cellophane film	glucose	5×10^{-4}–2×10^{-2} M	1 min	decrease of response at a rate of 2-3% per day	pH 6.6 (phosphate buffer), 30°	46
Lactate dehydrogenase	enclosure between electrode and dialysis film	lactic acid	10^{-4}–2×10^{-3} M	3-10 min	–	blood	50
Alcohol dehydrogenase	enclosure between electrode and cellophane film	methanol, ethanol	10^{-9}–2.5×10^{-8} M	2 min	decrease of activity by a factor exceeding 2 in 12 h	physiological buffer soln., pH 8.5	1

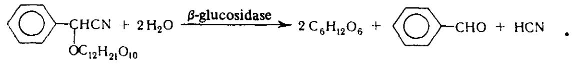
*The electrode was completely inactive.

In studies by Mosbach and coworkers[61] and Papariello et al.[62], enzyme electrodes were prepared by depositing a layer of the immobilised enzyme on a glass pH electrode, with the aid of which the concentration of hydrogen ions, formed as a result of the enzymatic reaction, was recorded. Enzyme electrodes for glucose[61] [reaction (9)], urea[61] [reaction (8)], and various penicillins[61,62] [reaction (10)] have been developed on the basis of this method:

$$\text{glucose} + O_2 + H_2O \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + H_2O_2; \quad (9)$$

$$\text{penicillin} + H_2O \xrightarrow{\text{penicillinase}} \text{penicilloic acid}. \quad (10)$$

Finally in 1971 Rechnitz and Llenado[63,64] described a new type of enzyme electrode in which a non-glass membrane was used as the electrochemical sensor. They developed[63,64] an analytical method for the determination of amygdalin using for this purpose a solid electrode consisting of a crystalline cyanide sensor coated by a layer of β-glucosidase immobilised in polyacrylamide gel. In the enzymatic hydrolysis of amygdalin [reaction (11)] the cyanide ions formed near the electrode as the reaction product diffuse through the layer of gel to the surface of the crystalline membrane and are recorded potentiometrically by the electrode system:



.(11)

The Table shows that the principal method used to immobilise the enzyme on the electrode involves its entrainment in a gel (in many cases the layer of the gel-enzyme was also covered by a cellophane film to reduce the diffusion of the enzyme from the gel into the solution). Approximately one-third of enzyme electrodes have been prepared by the simple entrainment of the enzyme between the electrode surface and the dialysis film. Finally, covalent binding of the enzyme to a carrier was used as the immobilisation method in only three investigations[45,46,58], but the authors noted a somewhat higher stability of enzyme electrodes with chemically combined enzymes compared with electrodes based on gel-enzymes.

The simplest method for the preparation of an enzyme electrode involves the mechanical entrainment of the enzyme between the sensor element of the electrode and the film membrane which retains the enzyme near the electrode but is permeable to substrate and product molecules (a dialysis film with definite pore dimensions is usually employed for this purpose). As a rule this enzyme immobilisation procedure does not impair the characteristics of the enzyme electrode relative to an enzyme immobilised in a gel on the surface of the sensor (see Table). Furthermore, it has been noted[54,56] that, in the determination of L-aminoacids with the aid of L-aminoacid oxidase, the gel-enzyme electrode was less stable and had a longer response time compared with the electrode coated by a thin layer of enzyme solution enclosed in a dialysis film. In addition, the authors[54] point out that riboflavin, added to the acrylamide solution as the polymerisation catalyst, inhibits L-aminoacid oxidase, which also impairs the electrode characteristics. On the other hand, the immobilisation of the enzyme in a polyacrylamide gel for electrodes based on D-aminoacid oxidase and asparaginase greatly increases their stability[55] (see Table). The attempts to immobilise the enzyme in a polyacrylamide gel for the glutaminase electrode resulted in a complete loss of activity by L-glutaminase[59], while the electrode covered by a dialysis film with an entrained thin layer of enzyme solution exhibited the normal response to the presence of L-glutamine in the mixture being analysed. Thus the available literature data so far do not allow one to give preference *a priori* to any one immobilisation procedure in the preparation of enzyme electrodes.

Almost all gel-enzyme electrodes about which there is at present information in the literature were prepared by immobilising enzymes in a polyacrylamide gel†. The

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† In the study by J. Kulis and B. Panavo, which is being carried out at the present time at the Institute of Biochemistry of Lithuanian SSR, an enzyme electrode has been developed for glucose in which glucose oxidase is immobilised on the surface of a polarographic platinum electrode in a copolymer of ethylene glycol methacrylate and ethylene glycol dimethacrylate acids (see Table)[69].

differences consist only in the method of polymerisation (chemical or photoinitiated) used to prepare the gel-enzyme. The advantages of polyacrylamide gels are that the polymer formed can be readily granulated, the polymerisation is rapid, and, dpending on the reaction conditions, it is possible to obtain gels with different porosities[24]. The methods for the immobilisation of enzymes in a polyacrylamide gel on the electrode surface have been described in detail by Montalvo and Guilbault[65].

VI. KINETIC ASPECTS OF THE OPERATION OF ENZYME ELECTRODES. FACTORS INFLUENCING THEIR RESPONSE

The quantitative determination of reagents in mixtures being analysed with the aid of enzyme electrodes can be achieved in principle in three different ways: (a) by continuing the enzymatic conversion of the substrate until completion and by recording the total change in electrode response as a result of the reaction; (b) by measuring the rate of change of the electrode response in the initial period of the enzymatic reaction (in other words by determining a quantity proportional to the initial reaction velocity); (c) by recording the change in electrode response from the beginning of the reaction to the attainment of a constant response (in consequence of the establishment of a steady-state concentration of the reaction product in the layer near the electrode).

The first procedure is probably the most accurate; it is not subject to the influence of effectors (enzyme inhibitors or activators), which may be present in the reaction mixture; the inactivation of the enzyme immobilised on the electrode occurring during the reaction does not affect the analytical results, merely increasing the time required for the analytical determination; finally, the calibration plot for this method should be linear regardless of the initial concentration of the reagent being determined. However, for a comparatively rapid analysis, it is necessary in this case to have electrodes with a low diffusional resistance of the reaction layer with respect to the substrate and the product and a very high concentration of the enzyme in the layer adjoining the electrode, which is usually difficult and frequently impossible under real conditions. This factor probably explains why this method has never been used for analytical determinations with the aid of enzyme electrodes.

The main disadvantage of the second analytical method is that the initial velocity of the enzymatic reaction depends hyperbolically on the substrate concentration:

$$v = \frac{k_{cat}[E]_0[S]_0}{K_m + [S]_0} \quad , \tag{12}$$

where k_{cat} is the catalytic constant and K_m the Michaelis constant for the enzymatic reaction proceeding in accordance with the general mechanism

$$E + S \overset{K_m}{\rightleftharpoons} ES \xrightarrow{k_{cat}} E + P \ . \tag{13}$$

Eqn. (12), called the Michaelis–Menten equation, shows that the initial velocity of the enzymatic reaction is a linear function of substrate concentration only in the region where $[S]_0 \ll K_m$.

Guilbault and Lubrano[46], who used the "initial velocity" method to determine the concentration of glucose with the aid of immobilised glucose oxidase, noted the speed of this method (the measurement of the initial velocities took 4–12 s under the experimental conditions[46]) and its reproducibility (the error was less than 2%). The advantage of the "initial velocity" method has also been noted by Guilbault and Nagy[58].

In the vast majority of different versions of analyses carried out using enzyme electrodes (see Table), the method based on recording the steady-state electrode response in the system has been used. The essential feature of the method is that the steady-state concentration of the enzymatic reaction products in the layer of immobilised enzyme on the electrode, which is recorded by the electrochemical sensor, is attained after a definite period from the instant of immersion of the electrode in the solution being analysed.

Consider the following model. We have a plane membrane with a thickness l covering the sensor element of the electrochemical device and containing the immobilised enzyme at a concentration $[E]_0$. The electrochemical device with the membrane is immersed in a substrate solution at a concentration $[S]_0$. The partition coefficients of the substrate and enzymatic reaction product between the membrane and solution are δ_S and δ_P respectively. It is necessary to find the relation between the steady-state electrode potential in the system and the initial concentrations of the substrate and the immobilised enzyme (taking into account diffusion factors). According to Fick's second law, the rates of diffusion of the substrate and product within the membrane in a direction x at right angles to its surface are $D_S \frac{d_2[S]}{dx^2}$ and $-D_P \frac{d^2[P]}{dx^2}$, where D_S and D_P are the diffusion coefficients of the substrate and product respectively. The rate of the enzymatic reaction in the membrane is determined by the Michaelis–Menten equation [Eqn. (12)]. In the steady state (with respect to diffusion) of the system, the rates of these two processes should be the same:

$$D_S \frac{d^2[S]}{dx^2} = \frac{k_{cat}[E]_0[S]}{K_m + [S]} \quad , \tag{14}$$

$$-D_p \frac{d^2[P]}{dx^2} = \frac{k_{cat}[E]_0[S]}{K_m + [S]} \quad , \tag{15}$$

where [S] and [P] are the concentrations of the substrate and product in the membrane.

Blaedel et al.[66] carried out a detailed analysis of this model. They showed that, at low substrate concentrations $[S] \ll K_m$, the steady-state concentration of the product in the layer of the membrane near the electrode is defined by Eqn. (16), provided that the reaction does not alter the concentration ratio in the overall bulk of the solution before the attainment of the steady state:

$$[P] = \frac{\frac{\alpha D_s \delta_p}{t_p}\sinh \alpha l + \frac{D_s}{D_p}\cosh \alpha l - \frac{D_s}{D_p}}{\frac{\cosh \alpha l}{\delta_s} + \frac{\alpha D_s}{t_s}\sinh \alpha l}[S]_0, \tag{16}$$

where t_S and t_P are the corresponding mass-transfer coefficients, and

$$\alpha = \sqrt{\frac{k_{cat}[E]_0}{K_m D_s}} \quad . \tag{17}$$

At high substrate concentrations $[S] \gg K_m$ the steady-state concentration of the product is

$$[P] = \frac{k_{cat}[E]_0 l^2}{2D_p} + \frac{\delta_p k_{cat}[E]_0 l}{t_p} . \tag{18}$$

Thus in the region where $[S] \ll K_m$ the steady-state concentration of the product in the layer near the electrode and hence the steady-state response of the enzyme electrode vary linearly with substrate concentration in solution [Eqn.(16)], while in the region where $[S] \gg K_m$ the steady-state concentration of the product is independent of the initial substrate concentration [Eqn.(18)]. Furthermore, it is seen from Eqn.(16) that the enzyme concentration in the membrane influences the steady-state concentration of the product only up to a certain limit. For high values of $[E]_0$, the steady-state electrode response ceases to depend on the concentration of the immobilised enzyme; in this case we have the limiting value $[P] = (\delta_p t_s / t_p)[S_0]$. Finally, the steady-state electrode response depends also on the Michaelis constant and the catalytic constant for the enzymatic reaction (which are in their turn influenced by pH, temperature, ionic strength, etc.), on the diffusion coefficients of the substrate and product, and on the thickness of the reaction layer.

According to the Nernst equation, in the presence of charged products of the enzymatic reaction the potential of the electrode system should vary logarithmically with the activity of the product. Assuming that the steady-state concentration of the product defined by Eqn.(16) is approximately equal to its activity under the experimental conditions, the Nernst equation can be written as follows:

$$E = E^0 + \frac{RT}{nF} \ln \left\{ \frac{\frac{\alpha D_s \delta_p}{t_p} \sinh \alpha l + \frac{D_s}{D_p} \cosh \alpha l - \frac{D_s}{D_p}}{\frac{\cosh \alpha l}{\delta_s} + \frac{\alpha D_s}{t_s} \sinh \alpha l} [S]_0 \right\}, \tag{19}$$

or, in the case of a singly-charged ionic product ($n = 1$):

$$E = E^0 + 0.0591 \log [S]_0. \tag{20}$$

It follows from Eqn.(20) that at low substrate concentrations one may expect a potential change of 59.1 mV for a tenfold change in the initial substrate concentration (at 25°C). However, for the majority of real systems the electrode response is not fully of the "Nernst" type. As examples, one may quote the experimental slopes of plots of E against lg $[S]_0$, which are 0.055 (determination of urea[66]), 0.050 (determination of urea[67]), and 0.048 (determination of amygdalin[64]). In the determination of various penicillins (see Table), the slope varies from 0.052 for ampicillin to 0.038 for dicloxacillin[62]; the authors were unable to explain this finding, but suggested that the differences between the responses of enzyme electrodes with respect to various penicillins may be due to the different thicknesses of the gel layer on the electrode surface.

In the determination of glutamine with the aid of an enzyme electrode[59], this slope was found to depend on the pH, varying from 0.048 (pH 6.0) to 0.040 (pH 5.0), which indicates, according to the authors, the influence of hydronium ions on the ion-selective electrode. Guilbault and Montalvo[67] found that the response of the electrode, on the surface of which immobilised urease had been deposited, in relation to a standard ammonium chloride solution actually exceeded the response of the usual glass electrode reversible with respect to ammonium ions. The authors[67] explained the higher sensitivity of the enzyme electrode by the fact that, under the experimental conditions (pH 7.0), urease is negatively charged, so that the enzyme immobilised on the electrode behaves similarly to a cation exchanger.

When the solution being analysed contains "interfering" ions, which also influence the electrode potential[57], the dependence of the potential on substrate concentration can be formulated as follows:

$$E = E^0 + \frac{RT}{F} \ln \left\{ \frac{\frac{\alpha D_s \delta_p}{t_p} \sinh \alpha l + \frac{D_s}{D_p} \cosh \alpha l - \frac{D_s}{D_p}}{\frac{\cosh \alpha l}{\delta_s} + \frac{\alpha D_s}{t_s} \sinh \alpha l} [S]_0^{1/n} + \sum_i \eta a_i^{1/z} \right\}, \tag{21}$$

where η is the ratio of the selectivities with respect to the ions, a_i the activity of the interfering ion, and z its charge. The potential of the enzyme pH electrode should in fact vary in accordance with this law if the hydrogen ions formed as a result of the enzymatic reaction are determined in buffer solutions.

Mossbach and coworkers[61], who investigated the operation of enzyme pH electrodes in buffer solutions at different concentrations, showed that urea may be determined with the aid of the urease electrode at phosphate buffer concentrations not exceeding 0.01 M. It is seen from Eqn.(21) that, when the substrate concentration is reduced, the electrode potential tends to the constant value

$$E = E^0 + \frac{RT}{F} \ln \left(\sum_i \eta a_i^{1/z} \right). \tag{22}$$

The electrode potential tends to the same value when the concentration of the enzyme immobilised on the electrode is reduced. Thus, the S-shaped relation between the potential of the enzyme electrode and the logarithm of the concentration of the substance being determined in solution, which is usually observed experimentally, can be readily accounted for with the aid of Eqns.(16)-(22).

A considerable proportion of enzyme electrodes described in the literature (see Table) are sensitive to ammonium ions[60]. A significant disadvantage of these electrodes is their response to virtually all univalent cations[54], which can be described by the following sequence[59]: $Ag^+ > H^+ > K^+ > NH_4^+ > Na^+ > Li^+$. The low selectivity of cation electrodes with respect to ammonium ions has so far precluded the quantitative analysis of biological liquids for aminoacids and urea (with the aid of immobilised aminoacid oxidases, asparaginase, glutaminase, and urease) without their preliminary treatment using exchangers[56-59]. However, Guilbault and Nagy recently reported an improvement of the selectivity of electrodes based on urease[57] and L-aminoacid oxidase[58] by the addition of the antibiotic nonactin to the layer of gel-enzyme. Under these conditions, the selectivity of the electrodes was expressed by the ratios $[NH_4^+]/[K^+] = 6.5$ and $[NH_4^+]/[Na^+] = 750$. Montalvo[68] also reported an appreciable increase of the selectivity of the cationic glass cation electrode following the deposition on its surface of a thin hydrophobic membrane (a siliconopolycarbonate film) which is permeable to ammonium ions.

Guilbault and Montalvo[67] studied in detail the factors influencing the response of the urease electrode. Almost all the observed effects are consistent with Eqns.(16)-(22). The authors[67] also showed that, when urease is immobilised in a polyacrylamide gel on the surface of a cation-responsive electrode, the thickness of the gel and its composition have almost no influence on the steady-state response of the enzyme electrode. Thus, when the thickness of the gel is reduced from 350 to 60 μm, the steady-state response diminishes only by 2%; variation of the gel concentration from 5 to 17.6% for a constant ratio of the concentrations of the monomer and the cross-linking agent leads to a change in the response smaller than 2%; finally, variation of the concentration of the cross-linking agent in the system from 5 to 19% at a constant gel concentration also leads only to a very small change in the response of the enzyme electrode[67].

VII. THE STABILITY OF ENZYME ELECTRODES

The stability of enzyme electrodes or their ability to retain the catalytic activity of the immobilised enzyme over a period of time varies over fairly wide limits depending on the type of enzyme and the nature of its immobilisation. The main disadvantage of the immobilisation of the enzyme in a gel is its gradual "elution" into the solution surrounding the enzyme electrode[52,57,64], which leads to a gradual decrease of the activity of the electrode. As a rule, the stability of such electrodes can be increased by placing around the layer of the gel-enzyme a thin cellophane (dialysis) film, which is readily permeable to substrate and product molecules, but not to enzyme molecules[52,56,67]. Electrodes with a higher enzyme concentration in the layer deposited on them are usually more stable[54,55]. The stability of enzyme electrodes containing immobilised D-aminoacid oxidase greatly increased when they were stored in a solution of flavin-adenine dinucleotide, which is a cofactor of the enzyme[55,60]. When asparaginase was immobilised in a polyacrylamide gel, the stability of the corresponding electrode greatly increased compared with that of the homogeneous enzyme (see Table); on the other hand, the stability of L-aminoacid oxidase immobilised in a gel was significantly lower than that of the soluble enzyme[54]. Finally, the immobilisation of glutaminase in a polyacrylamide gel, carried out in a study by Guilbault and Shu[59], led to the complete inactivation of the enzyme. Thus both these and other available literature data (see Table) do not allow an *a priori* choice of the immobilisation procedure for the preparation of a stable enzyme electrode.

The most detailed and systematic study of the stability of gel-enzyme electrodes prepared under different conditions has been carried out by Guilbault and Montalvo[67]. The following factors influencing the stability of the urease electrode were noted: (a) the concentration of urea in the test solution; (b) the concentration of the enzyme in the gel; (c) the initial activity of the immobilised enzyme; (d) the thickness of the layer of the gel-enzyme on the electrode; (e) the light intensity during photopolymerisation; (f) the duration of photopolymerisation in the preparation of the gel-enzyme; (g) the temperature of the gel-enzyme during photopolymerisation; (h) the type of enzyme electrode.

Guilbault and Montalvo[67] found the optimal conditions for the preparation of the gel-enzyme under which the stability of the immobilised urease is highest (the enzyme works periodically for 3 weeks without appreciable loss of activity). It was shown that the stability of the electrode depends on the urea concentration in the solution being analysed, becoming impaired with increasing substrate concentration. According to a number of data[56,60,67], an increase of the stability of the enzyme electrode is observed with increase of the thickness of the gel-layer (from 60 to 350 μm), with increase of the enzyme concentration in the reaction layer, and, finally, when the layer of gel-enzyme on the electrode is covered by a thin cellophane film.

Guilbault and Lubrano[46] made a comparative study of the stabilities of three types of electrodes with immobilised glucose oxidase—bound chemically to derivatives of polyacrylic acid, entrained in a polyacrylamide gel, and immobilised in a thin layer of solution between the surface of the electrode and a cellophane film. It has been noted[46] that the third type of electrode not only loses its activity appreciably on storage in a buffer solution but also its response diminishes in each successive determination of the glucose concentration in solution. For this reason, this type of electrode has not been used for the analytic determination of glucose (see Table). The response of enzyme electrodes of the first two types reaches a maximum after they have been working for 20–40 days and then diminishes during 200–300 days (see Table), the electrode with chemically immobilised glucose oxidase being more stable than the gel-enzyme electrode. The authors[46] suggest that the bell-shaped curve for the dependence of the electrode response on time may be accounted for by the superposition of two effects—the gradual formation of diffusion channels in the matrix of the immobilised enzyme and the simultaneous denaturation of the latter.

VIII. PROBLEMS AND PROSPECTS

The wide scale and effective application of immobilised enzymes in analytical chemistry requires the solution of a number of general biochemical problems (the development of methods for the isolation and purification of enzymes, the development of methods for the determination of the catalytic activities of specific enzymes, the study of the mechanisms of the action of specific enzymes, the elucidation of factors influencing enzyme activity, etc.). Apart from these problems, which have no direct bearing on the subject of the present review, the following problems must be solved for the development of highly specific and economical enzyme electrodes suitable for the selective determination of a wide range of chemical compounds:

(1) An increase of the stability of immobilised enzymes to such an extent that they can function for several months and years.

(2) The determination of universal immobilisation methods permitting immobilisation by standard procedures suitable for all enzymes (or for specific groups of enzymes).

(3) An increase of the specificity of ion-selective electrodes with respect to particular ions (for example ammonium ions), which will permit the quantitative determination of given reagents with the aid of the corresponding enzyme electrodes in the presence of extraneous ions.

(4) An increase of the sensitivity of electrochemical systems with respect to electrochemically active products of the corresponding enzymatic reactions. This will make it possible to extend the limits of the sensitivity of enzymatic analytical methods towards lower concentrations of the given reagents.

In order to assess the possibilities of enzymatic analytical methods and the prospects of their development, it is sufficient to quote a by no means complete list of reagents the quantitative determination of which is of interest for analytical chemistry and which can be determined with the aid of enzyme electrodes. These reagents include aliphatic and aromatic alcohols, aldehydes, acids, hydroxyacids, ketoacids, dicarboxylic acids, aminoacids, esters, amides, carboxylic acid nitriles, primary, secondary, and tertiary amines, diamines, glycols (including ethylene glycol, propane-1,2-diol, and butane-2,3-diol), glycerol, acetoin, acetoacetate, hydrazine, hydroxylamine, ethanolamine, tyramine, nitroethane and other aliphatic nitro-compounds, phenols, *o*- and *p*-dihydroxybenzenes, xanthine, hypoxanthine, cholesterol, androsterone and other 3-α-hydroxysteroids, testosterone and other 3-β- and 17-β-hydroxysteroids, 20-dihydrocortisone, penicillins, sugars, thiols, diisopropyl phosphorofluoridate and other organophosphorus compounds, DDT, hydrogen peroxide, nitrates, nitrites, sulphites, hydrogen sulphide, ammonia, nitric oxide, pyrophosphate, halides, cyanides, and metal ions (calcium, barium, zinc, cadmium, copper, manganese, cobalt, and nickel ions).

It is noteworthy that, in order to determine any of these reagents, one can select, in principle, a suitable chain of coupled enzymatic reactions, with the substance to be determined at the beginning and the electrochemically active enzymatic reaction product at the end. In other words, in principle, a suitable enzyme electrode can be prepared for the quantitative determination of virtually any of the reagents enumerated above.

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The Quenching of Singlet Oxygen

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The kinetics and mechanisms of processes involving the quenching of oxygen in the singlet state ($^1\Delta_g$) are examined. The rate constants for the deactivation of singlet oxygen in various solvents, for the reactions of singlet oxygen with unsaturated and aromatic compounds, and for processes involving the quenching of singlet oxygen by amines, metal complexes, and certain other compounds have been compiled. The influence of the polymer matrix on the reactivity of electron acceptors and the efficiency of quenching agents is considered and the role of singlet oxygen in photochemical oxidation reactions of low- and high-molecular-weight organic compounds is discussed.
The bibliography includes 77 references.

CONTENTS

I. INTRODUCTION

It was shown in 1964[1,2] that many photosensitised oxidation reactions proceed with participation of oxygen in an electronically excited singlet state and that "singlet" oxygen can give rise to oxidation products in nearly theoretical yields. These studies aroused much interest and stimulated theoretical and practical investigations of the properties and reactions of singlet oxygen. Among practical problems, the possibility of using singlet oxygen in preparative organic chemistry, the problem of smog and the pollution of the atmosphere, and the problem of protection of biological systems as well as low-molecular-weight and high-molecular-weight compounds from photosensitised oxidation have attracted particular attention.

In connection with the problem of improving the resistance of organic compounds to photochemical oxidation, questions concerning the efficiency of the quenching of singlet oxygen and the mechanism of the action of quenching agents are considered here. A number of recent reviews[3-9] of the properties and reactions of singlet oxygen may be recommended.

II. KINETICS OF PHOTOCHEMICAL OXIDATION BY SINGLET OXYGEN

In photosensitised oxidation reactions the main source of singlet oxygen ($^1O_2$) is believed to be the reaction involving the quenching of the triplet state of the sensitiser ^3S by oxygen in the ground state $^3O_2$:

$$^3S + {}^3O_2 \rightarrow {}^1S_0 + {}^1O_2, \qquad (1)$$

where $^1S_0$ is the ground singlet state of the photosensitiser. Other reactions are also known:

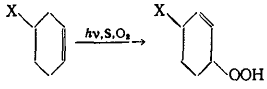
$$^1S_1 + {}^3O_2 \rightarrow {}^1S_0 + {}^1O_2, \qquad (2)$$

$$^1S_1 + {}^3O_2 \rightarrow {}^3S + {}^1O_2, \qquad (3)$$

where $^1S_1$ is the excited singlet state of the photosensitiser. However, the probability of these reactions is as a rule lower than that of reaction (1).

1. Characteristic Reactions of Singlet Oxygen

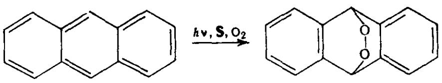
(a) Oxidation of olefins containing an allylic hydrogen atom to hydroperoxides. A characteristic shift of the double bond to the allylic position takes place in the reaction, for example:



(4)

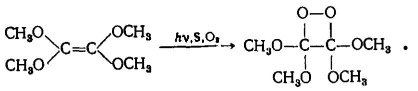
where X is a substituent.

(b) The addition of $^1O_2$ to diene hydrocarbons with formation of cyclic peroxides, for example:



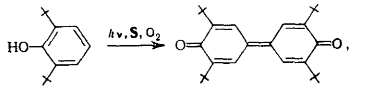
(5)

(c) Addition to olefins having an excess electron density at the double bond with formation of 1,2-dioxetans, for example:



$$(CH_3O)_2C{=}C(OCH_3)_2 \xrightarrow{h\nu,S,O_2} CH_3O{-}\overset{O-O}{\underset{CH_3O}{C-C}}{-}OCH_3\,. \qquad (6)$$

(d) The interaction of $^1O_2$ with reducing agents, for example phenols[10], sulphur-containing compounds[4,11,12], and amines[4,13-15], for example:

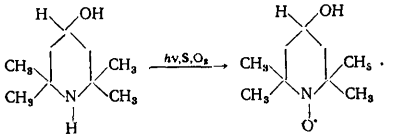


(7)

$$2\,(C_2H_5)_2\,S \xrightarrow{h\nu,S,O_2} 2\,(C_2H_5)_2\,SO, \qquad (8)$$

$$2\,(CH_3)_2\,SO \xrightarrow{h\nu,S,O_2} 2\,(CH_3)_2\,SO_2, \qquad (9)$$

$$H_2NCH_2CH_3 \xrightarrow{h\nu,S,O_2} H_2NCH\,(OOH)\,CH_3, \qquad (10)$$

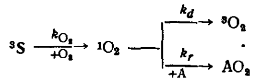


(11)

2. Kinetics of Oxidation in the Absence of Quenching Agents

The oxidation of compounds containing double bonds by singlet oxygen is hardly influenced by effective inhibitors of radical-chain oxidation processes, for example 2,6-di-t-butyl-4-methylphenol. On the other hand, tertiary aliphatic amines, which are typical $^1O_2$ quenching agents, do not inhibit the radical-chain oxidation of tetralin by molecular oxygen[16]. Thus, the oxidation by singlet oxygen of compounds with double bonds does not proceed via a radical-chain mechanism.

The kinetic scheme for the oxidation of an acceptor A can be formulated as follows:



$$ {}^3S \xrightarrow[+O_2]{k_{O_2}} {}^1O_2 - \left| \begin{array}{l} \xrightarrow{k_d} {}^3O_2 \\ \xrightarrow[+A]{k_r} AO_2 \end{array} \right. \tag{12} $$

Hence

$$ \frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^1O_2}} \left(1 + \frac{k_d}{k_r} \cdot \frac{1}{[A]} \right), \tag{13} $$

where Φ_{AO_2} and Φ^1O_2 are the quantum yields of the oxidation product AO_2 and of the formation of singlet oxygen respectively. Mechanism (12) can be used not only to describe reactions involving the addition of singlet oxygen to unsaturated compounds [reactions (4)–(6)] but also other reactions of singlet oxygen. Thus, it has been shown recently that the reactions of singlet oxygen with secondary and tertiary amines[15], in which a free valence is produced, are also fully described by scheme (12).

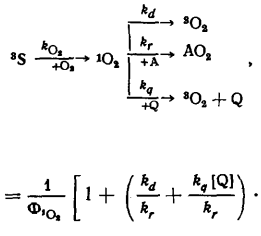
It is clear from Eqn. (13) that the yield of product is determined by the ratio of the rates of deactivation of $^1O_2$ and of the interaction of $^1O_2$ with the acceptor A. The maximum yield $\Phi_{AO_2} = \Phi^1O_2$ is reached under the following condition:

$$ k_r[A] \gg k_d. $$

The use of Eqn. (13) makes it possible to determine k_r/k_d—the relative reactivity of the acceptor towards $^1O_2$—from the dependence of the quantum yield on the concentration of the acceptor.

3. Kinetics of Oxidation in the Presence of Quenching Agents

In the presence of a quenching agent Q for singlet oxygen, the kinetic scheme for the oxidation of the acceptor becomes



$$ {}^3S \xrightarrow[+O_2]{k_{O_2}} {}^1O_2 \left| \begin{array}{l} \xrightarrow{k_d} {}^3O_2 \\ \xrightarrow[+A]{k_r} AO_2 \\ \xrightarrow[+Q]{k_q} {}^3O_2 + Q \end{array} \right. , \tag{14} $$

whence

$$ \frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^1O_2}} \left[1 + \left(\frac{k_d}{k_r} + \frac{k_q[Q]}{k_r} \right) \cdot \frac{1}{[A]} \right]. \tag{15} $$

It follows from Eqn. (15) that the variation of Φ_{AO_2} with [A] should be represented by a straight line when $1/\Phi_{AO_2}$ is plotted against 1/[A], and the parameters k_r/k_d and k_r/k_q, characterising the relative reactivities of the acceptor and the quenching agent in relation to $^1O_2$ respectively, may be determined from the dependence of the slope on [Q].

In the kinetic schemes (12) and (14) it was assumed that $\Phi^1O_2 = \Phi^3S$. However, these quantities are not equal when A or Q interacts with ^3S. If, for example, Q quenches only ^3S (with a rate constant k_Q) and not $^1O_2$, then

$$ \frac{1}{\Phi_{AO_2}} = \frac{1}{\Phi_{^3S}} \left(1 + \frac{k_q[Q]}{k_{O_2}[O_2]} \right) \left(1 + \frac{k_d}{k_r[A]} \right). \tag{16} $$

Like Eqn. (15), Eqn. (16) represents a linear plot of $1/\Phi_{AO_2}$ against 1/[A]. However, in contrast to Eqn. (15), the intercept on the ordinate axis depends on [Q]. Furthermore, the slope of the plot defined by Eqn. (16) depends on $[O_2]$. Quenching of the triplet state of the photosensitiser can be distinguished from the quenching of singlet oxygen by means of these features.

The use of Eqns. (13) and (15) makes it possible to obtain the kinetic parameters k_r/k_d and k_q/k_d from the concentration variation of the quantum yield and k_r/k_q from the concentration variation of the rate of oxidation.

4. The Efficiency of Quenching Agents in Liquid-Phase Systems

In order to obtain absolute values of the kinetic constants characterising the efficiency of quenching agents and the reactivities of singlet oxygen acceptors, the kinetics of the oxidation reactions were investigated and measurements were made of the lifetimes of singlet oxygen in various solutions using flash photolysis[17-25].

Table 1. The constants k_d for various solvents.

Solvent	$10^{-3}k_d$, s^{-1}	Refs.	Solvent	$10^{-3}k_d$, s^{-1}	Refs.
Water	350	21	Cyclohexane	41	21
D_2O	350	21	Isooctane	40	22
Dimethylformamide	140	19	4:1 benzene-methanol	38	23
Methanol	100	21	Pyridine	31	23
	100	11	t-Butyl alcohol	30	23
	(a) 88	23	Dioxan	29	23
	(b) 97	23	Benzene	28	21
	200	19		80	19
1:1 Methanol-t-butyl alcohol	(c) 60	26	Acetonitrile	23	21
			Chloroform	12	21
Ethanol	58	21	Methylene chloride	7,3	22
	180	19	Carbon tetrachloride	1	21
n-Butyl alcohol	52	23			
4:1 Bromobenzene-methanol	43	23			

Note: a) and b) Methylene Blue and Rose Bengal were used respectively as photosensitisers; c) estimated from data in this Table and those of Higgins et al.[26]

It follows from mechanism (12) that there is competition between reactions involving the spontaneous destruction of $^1O_2$ and its interaction with acceptors. Table 1 shows that the values of k_d change very markedly on passing from one solvent to another. These constants are large and correspond to the lifetimes of $^1O_2$ in various solvents ranging from a microsecond to a millisecond. For effective oxidation, the oxygen must be able to react with acceptors during this period; consequently, the rate constant k_r must also be large. It is seen from Eqn. (13) that the fraction η of singlet oxygen interacting with the acceptor is 0.5 when $k_d = k_r[A]$ or

$$ [A]_{\eta=0.5} = \frac{k_d}{k_r}. \tag{17} $$

Eqn. (17) shows clearly at which acceptor concentration or for which values of the kinetic constants the spontaneous destruction of oxygen and the oxidation process proceed at comparable rates.

Table 2. The constants k_r for the reactions of singlet oxygen with olefins in solutions.

Compound	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Non-1-ene	Methanol	(a) 7.5×10^2	27
4-Methylcyclohexene	Methanol	(a) 5×10^3	27
Cyclohexene	Methanol	(a) 7.5×10^3	27
2,3-Dimethylbut-1-ene	Methanol	(a) 1.5×10^4	27
Hex-2-ene	Methanol	(a) 6.5×10^4	27
Cyclopentene	Methanol	(a) 1×10^5	27
2,3-Dimethylcyclohexene	Methanol	(a) 3.5×10^5	27
1-Methylcyclohexene	Methanol	(a) 3×10^5	27
2-Methylbut-2-ene	1:1 Methanol–t-butyl alcohol	(b) 5×10^5	26
2-Methylpent-2-ene	Pyridine	(c) 6×10^5	28
p-Chlorotrimethylstyrene	t-Butyl alcohol	(d) 6×10^5	26
1-Methylcyclopentene	Methanol	(e) 8×10^5	29
Cyclohexadiene	1:1 Methanol–t-butyl alcohol	(b) 5×10^5	26
	Methanol	(a) 2.5×10^6	27
Cyclopentadiene	Methanol	(e) 1×10^7	30
1,2-Dimethylcyclohexene	Methanol	(e) 3×10^7	30
2,3-Dimethylbut-2-ene	Methanol	(a) 2×10^7	27
	Methanol	(a) 4×10^7	27
	Methanol	(e) 3×10^7	30
	Methanol	(e) 2×10^7	31
	Methanol–t-butyl alcohol	(b) 2×10^7	26
β-Carotene	Benzene	(f) 1.3×10^{10}	25
	Benzene	(f) 2×10^{10}	21
	4:1 Benzene–methanol	(f) 3×10^{10}	11

Note: a) Recalculated directly from relative values based on $k_r = 4 \times 10^7$ for 2,3-dimethylbut-2-ene; b) recalculated on the basis of $k_d = 6 \times 10^4$; c) recalculated on the basis of $k_q = 1 \times 10^7$ for triethylamine; d) recalculated on the basis of $k_d = 3 \times 10^4$; e) recalculated on the basis of $k_d = 1 \times 10^5$; f) the value of k_q.

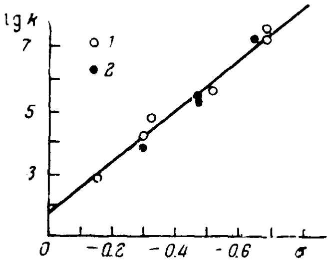


Figure 1. Dependence of the logarithms of the rate constants for the reactions of olefins with singlet oxygen on the σ_n constants of the substituents; 1) acyclic olefins; 2) cyclohexene derivatives.

The values of k_r for certain olefins and aromatic compounds are listed in Tables (2) and (3). It is seen that they depend very markedly on the structure of oxygen acceptors. On the other hand, the dependence of k_r on the nature of the solvent is comparatively slight. Fig. 1 shows that the influence of substituents on k_r can be described by the Hammett equation†.

The rate constants for the quenching of singlet oxygen by amines and their derivatives as well as by organometallic compounds are compiled in Tables 4 and 5. The rate constants for quenching by β-carotene are listed in the last rows of Table 2; the tables show that the rate constants for quenching by β-carotene and certain organometallic compounds are equal or close to diffusional constants. The constants k_q are very large for many amines. They can be described by the Hammett equation (see, for example, Young and coworkers[39,40]).

Table 3. The constants k_r for the reactions of singlet oxygen with aromatic compounds in solutions.

Compound	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Anthracene	Benzene	(a) 7×10^4	33
	Benzene	(a) 5×10^4	34
	8:1 Benzene–ethanol	(b) 9×10^4	58
9,10-Diphenylanthracene	Benzene	(a) 5×10^5	33
	Benzene	(a) 6×10^5	34
	Pyridine	(c) 8×10^6	35
Naphthacene	Methylene chloride	1.8×10^7	36
	8:1 Benzene–ethanol	(b) 7×10^6	15
9,10-Dimethylanthracene	Pyridine	(c) 4×10^6	35
Rubrene	Pyridine	(c) 9×10^7	35
	—	7×10^7	22
	Benzene	(a) 3×10^7	37
	Benzene	(a) 2×10^7	33
2-Phenylfuran	Methanol	(d) 6×10^7	31
2-Methylfuran	Methanol	(d) 9×10^7	31
2,5-Diphenylfuran	Methanol	(d) 1×10^8	31
	Methanol	4.5×10^7	23
2,5-Dimethylfuran	Methanol	(d) 4×10^8	31
	Methanol	(d) 1×10^8	30
	1:1 Methanol–t-butyl alcohol	(e) 5×10^7	26
	Water	1.5×10^9	38
1,3-Diphenylisobenzofuran	t-Butyl alcohol	0.6×10^9	23
	4:1 Bromobenzene–methanol	0.7×10^9	23
	n-Butyl alcohol	0.8×10^9	23
	4:1 Benzene–methanol	0.9×10^9	23
	4:1 Benzene–methanol	1.5×10^9	25
	Methanol	1.3×10^9	23
	Methanol	0.7×10^9	17
	Pyridine	2.1×10^9	23

Note: a) Recalculated on the basis of $k_d = 2.8 \times 10^4$; b) recalculated on the basis of $k_r = 4 \times 10^7$ for dimethylanthracene; c) recalculated on the basis of $k_r = 4 \times 10^7$ for 2,3-dimethylbut-2-ene; d) recalculated on the basis of $k_d = 1 \times 10^5$; e) recalculated on the basis of $k_d = 6 \times 10^4$.

In contrast to the constants k_r for olefins and aromatic compounds, the constants k_q for amines can depend markedly on the solvent. However, the nature of the dependence is determined by the structure of the amine. For example, *NN*-dimethylaniline and methylamine quench $^1O_2$ in methanol more effectively than in Freon 113 ($C_2Cl_3F_3$) by three orders of magnitude. On the other hand, the rate constants for quenching by diethylamine and triethylamine differ only by a factor of several units in the same solvents.

Above it was already noted that phenols, azides, and sulphur-containing compounds can behave as quenching agents for singlet oxygen. The kinetic constants for a very small number of compounds of these classes are known. Thus $k_q = 2.2 \times 10^8$ for NaN_3 in methanol[45], $k_q \leqslant 7 \times 10^7$‡ for hydroquinone in a 4 : 1 benzene–methanol

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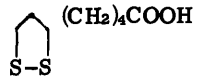
† In the example quoted, the σ_n constants of the substituents were used to construct the correlation plot.

‡ Quenches also ^3S.

mixture[11], $k_q = 6 \times 10^6$ for diethyl sulphide in the same solvent[11], and $k_r = 1 \times 10^8$ § for lipoic acid



in benzene[37].

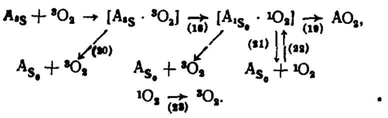
Table 4. The rate constants k_q for the quenching of singlet oxygen by amines and their derivatives in the liquid phase.

Compound	Solvent	k_q, litre mole^{-1} s^{-1}	Refs.
Isopropylamine	Methanol	4.5×10^4	39
Cyclohexylamine	Methanol	8×10^4	39
Pyrrolidine	Methanol	2×10^5	39
Benzylamine	Methanol	2.5×10^5	39
t-Butylamine	Methanol	6.5×10^5	39
Piperidine	Methanol	9×10^5	39
Piperazine	Methanol	1×10^6	39
Nicotine	Methanol	(b) 1.5×10^6	28
Diethylamine	Methanol	2×10^6	39
Diphenylamine	Methanol	6×10^6	39
Diazabicyclo[2,2,2]octane (DABCO)	Methanol	7.5×10^6	39,40
	4:1 Benzene–methanol	1.5×10^7	11
	n-Butyl alcohol	4.5×10^6	40
	Isooctane	3.5×10^7	22
	Methylene chloride	3.5×10^7	22
Triethylamine	Methanol	(c) $1. \times 10^7$	40
4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical	1:1 Benzene–methanol	(b) 1.5×10^7	41
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine	Methylene chloride	(d) 5×10^7	36
1,2,2,6,6-Pentamethylpiperidin-4-yl-nonadecanoate	1:1 Benzene–ethanol	(e) 3×10^7	42
1,2,2,6,6-Pentamethylpiperidin-4-yl-(3,5-di-t-butyl-4-hydroxyphenyl)-*β*-propionate	1:1 Benzene–ethanol	(e) 7×10^7	42
	Methanol	1×10^8	39
NN-Dimethylaniline		(a) 7.5×10^7	23
	$C_2Cl_3F_3$ (Freon 113)	2×10^5	20
		(a) 8×10^7	43
β-Naphthylamine	Ethanol	3.5×10^8	44
N-Isopropyl-*N*′-phenyl-*p*-phenylenediamine	Isooctane	(f) 6×10^8	43
NNNN′-Tetramethylphenylenediamine	Methanol	6×10^8	39
N-Cyclohexyl-*N*-phenyl-*p*-phenylenediamine	Ethanol	(g) 5×10^8	–
o-Phenylenediamine	2-Butoxyethanol	(f) 5×10^9	22
	Ethanol	(f) 3×10^8	43

Note: a) solvent not indicated; b) obtained on the basis of $(k_q)_{DABCO} = 1 \times 10^7$; c) according to Smith[28], in pyridine $(k_q)_{DABCO} \simeq (k_q)_{triethylamine}$; d) obtained on the basis of $k_d = 7.3 \times 10^3$; e) estimated from Felder and Schumacher's data[42] on the basis of $(k_q)_{DABCO} \simeq 1 \times 10^7$; f) recalculated from the relative rates on the assumption that $k_q = 5 \times 10^8$ for *N*-cyclohexyl-*N*-phenyl-*p*-phenylenediamine; g) the rate constants have been adopted on the basis of data in the preceding two rows; h) obtained on the basis of $k_d = 4 \times 10^5$ for 2-butoxyethanol[22].

5. The Influence of the Polymer Matrix on the Kinetics of the Quenching Processes and Their Rate Constants

In the kinetic schemes for oxidation by singlet oxygen considered above, it was assumed that $^1O_2$ is formed as a result of interaction with the photosensitiser. However, photochemical reactions in which singlet oxygen is formed in a reaction involving the substance being oxidised (excited by light) and then itself interacts with the latter are well known and have been investigated in detail[46]:



(18)-(23)

Table 5. The rate constants k_q for the quenching of singlet oxygen by organometallic compounds in the liquid phase*.

Quenching agent	Solvent	k_q, litre mole^{-1} s^{-1}	Refs.
Nickel(II) 3,5-di-t-butyl-4-hydroxybenzoate	1:1 Benzene–ethanol	8×10^6**	42
Ferrocene	Benzene	9×10^6	25
Bismuth(III) dimethyldithiocarbamate	Methylene chloride	1×10^7	36
Nickel(II) bis(butyl-3,5-di-t-butyl-4-hydroxybenzylphosphonate)	Methylene chloride	1.4×10^7	22
	1:1 Benzene–ethanol	8×10^6**	42
	Methylene chloride	6×10^6	36
Zinc(II) bis(n-butyldithiocarbamate)	Carbon disulphide	2×10^7	24
Nickel(II) acetylacetonate	Methylene chloride	7.5×10^7	44
Nickel(II) bis[2,2′-thiobis(4-t-octylphenoxide)]	Isooctane	1.3×10^8	22
(n-Butylamine)nickel(II) bis[2,2′-thiobis(4-t-octylphenoxide)]	Carbon disulphide	1.5×10^8	24
	Isooctane	1.8×10^8	22
Nickel(II) bis[2,2′-thiobis-(4-t-octylphenoxide)]	Carbon disulphide	5×10^8	24
Cobalt(II) diisopropyldithiocarbamate	Methylene chloride	1.9×10^9	44
Nickel(II) bis-(2-hydroxy-5-methoxyphenyl-*N*-n-butylaldimine)	Isooctane	2.4×10^9	44
Bis-(2-hydroxy-4-methylphenyl undecyl ketone oximato)nickel(II) (Negopex B)	Benzene	2.7×10^9	25
Bis-(2-hydroxy-4-methylacetophenone oximato)nickel(II) (Negopex A)	Benzene	3×10^9	25
Palladium(II) N-hydroxyformheptadecylimidoyl-4-t-butylphenoxide	Benzene	6×10^7	25
Nickel(II) diisopropyldithiocarbamate	Methylene chloride	3.4×10^9	44
Iron(III) diisopropyldithiocarbamate	Methylene chloride	3.8×10^9	44
Nickel(II) diisopropyl phosphorodithioate	Methylene chloride	5.4×10^9	44
Nickel(II) di-n-butyldithiocarbamate	Carbon disulphide	4×10^9	24
	Isooctane	7×10^9	22
	Methylene chloride	3.5×10^9	36

Note: * Several new studies, in which the values of k_q were determined for a large number of transitional metal complexes, have been published recently[75-77]; the most effective of these quench singlet oxygen with nearly diffusional rate constants[77].
** Estimated from Felder and Schumacher's data[42] on the basis of $(k_q)_{DABCO} = 1 \times 10^7$.

Here singlet oxygen is formed in a reaction with the acceptor $A_{^3S}$ in the excited triplet state. A characteristic feature of this scheme is that the complex $A_{S_0} \cdot {}^1O_2$, the precursor of the product AO_2, is formed in two different reactions: in reaction (18) within a cage, designated by brackets (at the point of encounter of $A_{^3S}$ and $^3O_2$), and in reaction (22) between an unexcited acceptor molecule and singlet oxygen which has emerged from the cage into the bulk phase.

It is readily seen that, for the specified values of the kinetic constants, the kinetic law governing the reaction is determined by the concentration of A. In the region of very low values of [A] the complex $A_{S_0} \cdot {}^1O_2$ is formed exclusively via reaction (18) and the reaction involving the formation of AO_2 is of first order with respect to the substance oxidised.

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§ It has not yet been established whether lipoic acid reacts with $^1O_2$ or whether it behaves as a quenching agent[37].

The $^1O_2$ species which have emerged from the cage [reaction (21)] are destroyed in reaction (23) without having sufficient time to react with A [reaction (19)], since the distances between the species A are very small. In the region of very high concentrations [A], the complex $A_{S_0}.^1O_2$ is formed via reactions (18) and (22). Having emerged from the cage each species $^1O_2$ reacts with A, and therefore the quantum yield is independent of [A]. In the region of moderate concentrations the complex $A_{S_0}.^1O_2$ is also formed via reactions (18) and (22), but the quantum yield increases with increase of [A]; the order of the reaction with respect to the substance oxidised is intermediate between first and second.

It has recently been shown[47-49] that, when the photochemical reaction is carried out in a polymer matrix, the kinetics are different: the order of the reaction with respect to the substance oxidised is much higher than the second and the reaction is rapidly retarded. As an example, Fig. 2 presents kinetic curves for the variation of the concentration of anthracene dissolved in a polystyrene film, in photochemical oxidation under the influence of light at a wavelength of 365 nm in air at room temperature. If irradiation is stopped at some instant, the specimen is heated at 95–100°C for 15–20 min in the dark, cooled to room temperature, and then irradiation is continued, the reaction starts again (curve *2*) and is again retarded under the conditions of continuous irradiation. With periodic and fairly frequent heating after irradiation (thermal activation), the reaction is faster (curve *3*) and follows liquid-phase kinetics.

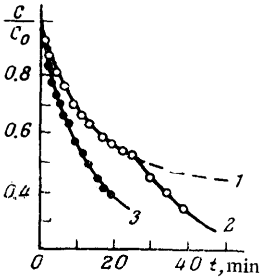


Figure 2. Variation of the concentration of anthracene C (initial concentration $C_0 = 2.8 \times 10^{-3}$ M) in a polystyrene film during irradiation in air with light at a wavelength of 365 nm: 1) continuous irradiation; 2) repeated irradiation after 10-min heat treatment at 100°C; 3) periodic conditions: after the determination of each experimental point indicated on the curve, the system was heated at 100°C for 10 min.

In general terms, the effect involving the rapid inhibition and arrest of the reaction can be accounted for by the fact that the polymer is an inhomogeneous system and therefore the probabilities of photochemical oxidation are not the same at various points within it. Species located at the points where the quantum yield is highest react initially, the quantum yield decreasing gradually in the course of the reactions. In order to describe the inhomogeneity of the polymer and the influence of the polymer matrix on the oxidation kinetics, a model has been proposed[48,49] according to which the substrate molecules in the polymer are located together with oxygen molecules in cages which differ in their permeability to oxygen. Within the framework of this model, the probability of the photochemical reaction is higher at low substrate concentrations for low permeability of the cage, since an increase of the lifetime of the A–$^1O_2$ pair corresponds to a decrease of permeability. On the other hand, at high concentrations of the acceptor A in the region corresponding to the preferential occurrence of the bimolecular reaction, species in cages with a high permeability react first. In this model the inhibition of the reaction is attributed to the gradual consumption of the species located in the regions of the polymer matrix more favourable for the reaction and thermal activation is accounted for by the restoration of the initial distribution of the substrate among the cages with different permeabilities as a result of the increase of the intensity of molecular motion at elevated temperatures. On the basis of the concepts described above, a quantitative theory of such self-inhibiting processes, involving oxidation by singlet oxygen, has been devised[49] for various selected laws governing the distribution of the cages with respect to permeability.

Table 6. Comparison of the kinetic constants for a solution (in methylene chloride) and a polymer (polystyrene) at room temperature[36].

Compound	Methylene chloride		Polystyrene		$\frac{(k_q/k_d)_L}{(k_q/k_d)_S}$	$\frac{(k_r/k_d)_L}{(k_r/k_d)_S}$
	$k_q \cdot k_d$, litre mole^{-1}	k_r/k_d, litre mole^{-1}	k_q/k_d, litre mole^{-1}	k_r/k_d, litre mole^{-1}		
β-Carotene	$3.6 \cdot 10^6$	—	$8 \cdot 10^3$	—	450	—
Nickel dibutyldithiocarbamate	$4.7 \cdot 10^5$	—	$1.1 \cdot 10^3$	—	420	—
Rubrene	—	$9 \cdot 10^3$	—	70	—	140
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine	$7.3 \cdot 10^3$	—	$4.2 \cdot 10^2$	—	17	—
Tetracene	—	$2.5 \cdot 10^3$	—	50	—	50
Bismuth dimethyldithiocarbamate	$1.5 \cdot 10^3$	—	$2.4 \cdot 10^2$	—	6	—
Nickel(II) bis-(3,5-di-t-butyl-4-hydroxybenzylphosphate)	$5.1 \cdot 10^2$	—	$1.7 \cdot 10^2$	—	3	—
Anthracene	—	1.8	—	0.25	—	7

Note: The subscripts L and S denote the liquid and solid phases respectively (Ed. of Translation).

The first values of the rate constants for the quenching and oxidation processes[36] showed that the polymer matrix has a significant influence on these processes (Table 6). The correlation between the constants in the liquid and solid phases and the levelling of the kinetic constants for the solid phase are the most striking features. For example, the highest value of k_q/k_d for polystyrene is 50 times higher than the lowest value, whereas the corresponding values for methylene chloride differ by a factor of 5000. In other words, the efficiencies of various quenching agents differ much less in the solid phase than in the liquid phase. A similar levelling phenomenon was observed previously for the reactivities of various antioxidants in relation to peroxy-radicals in solid polystyrene[50]. In this case the levelling was accounted for by the dependence of the rate of the chemical reaction both on the reactivity of the antioxidants and on the mobility of the reactants in the polymer matrix. It is at present difficult to say whether this mechanism can be extended also to the $^1O_2$ quenching reactions, since there are few experimental data.

The data in Table 6 create the impression that the efficiency of the most powerful quenching agent is disproportionately reduced in the polymer matrix. Experiments with rubrene, tetracene, and anthracene also revealed that, on passing from the liquid to the solid phase, the values of k_q decrease less than those of k_r.

In polystyrene the quenching of $^1O_2$ by nickel(II) dibutyldithiocarbamate, bismuth(III) dimethyldithiocarbamate, and the nickel(II) salt of 3,5-di-t-butyl-4-hydroxybenzylphosphonic acid in polystyrene is not accompanied by a change in the absorption spectra of these substances. Their concentrations hardly change, which means that in both the solid polymer and in solutions the compounds quench $^1O_2$ via a physical mechanism.

III. THE QUENCHING MECHANISM

1. Quenching via Charge Transfer

Ideas about the quenching mechanism have been developed[51] on the basis of the observed correlation between the values of k_q for the gas phase and the ionisation potentials I_p of the quenching agents (amines). Later similar correlations were found for quenching by sulphur-containing compounds in the gas phase (Table 7) and by amines in the liquid phase (Table 8).

Table 7. The ionisation potentials of sulphur-containing compounds and the rate constants for the gas-phase quenching of $^1O_2$ by these compounds[12].

Quenching agent	I_p, eV	k_q, litre mole^{-1} s^{-1}
Methanethiol	9.44	$2.3 \cdot 10^3$
Dimethyl disulphide	9.05	$1.0 \cdot 10^4$
Thiophen	8.86	$3.6 \cdot 10^4$
Dimethyl sulphide	8.69	$1.6 \cdot 10^5$
Diethyl sulphide	8.42	$4.1 \cdot 10^5$

These correlations led to the conclusion that quenching takes place via the formation of a charge-transfer complex in which $^1O_2$ behaves as the electron acceptor[51]. This complex is formed only at the instant of collision and is not in equilibrium with the reactants. This is evident from the fact that the rate constant for the quenching of $^1O_2$ by amines (A) in the gas phase increases with temperature[51]. For an "equilibrium" complex, one might have expected the opposite relation, since an increase of temperature leads to a decrease of its equilibrium concentration.

The overall equation for the quenching process

$$^1O_2 + {}^1A_0 \rightarrow {}^3O_2 + {}^1A_0 \tag{24}$$

shows that it takes place with a change in the overall spin and therefore its probability should be reduced, according to Wigner's rule, particularly since the system considered here does not contain either heavy atoms or paramagnetic quenching agents or catalysts, which reduce the degree of prohibition as a result of spin–orbit interaction. However, it is believed[51] that, in a $^1O_2$–quenching agent system in the singlet state, even weak spin–orbit interactions are sufficient to reverse the spin.

The initial state of the $^1O_2$–$^1A_0$ system can be regarded as a superposition of the unperturbed singlet state of the complex $^1O_2.^1A_0$ and the singlet state of the charge-transfer complex $\lambda(^1CT)$, where λ indicates to what extent the compound $^1O_2.^1A_0$ has the properties of a charge-transfer complex. Accordingly, the final state may be represented as a superposition of the triplet state of the complex $^3O_2.^1A_0$ and the charge-transfer triplet state $\mu(^3CT)$. Since the singlet and triplet states of the charge-transfer complex differ little in energy, even a weak spin–orbit interaction between the singlet and triplet charge-transfer states (involving, for example, nitrogen or sulphur atoms) can convert the initial and final states into states with "mixed" multiplicity and thus allow at least partially the transition

$$^1[^1O_2 \cdot {}^1A + \lambda\,(^1CT)] \rightarrow {}^3[^3O_2 \cdot {}^1A + \mu\,(^3CT)]. \tag{25}$$

From this point of view, the observed correlation between the quenching rate constants and the ionisation potentials can be accounted for by the increase of the contribution of the charge-transfer states in the initial and final systems and by the corresponding increase of the mixing of states with different multiplicities[51].

Table 8. The rate constants for the quenching of $^1O_2$ by amines in methanol solution[39].

Quenching agent	I_p, eV	$k_q \cdot 10^{-6}$, litre mole^{-1} s^{-1}	Quenching agent	I_p, eV	$k_q \cdot 10^{-6}$, litre mole^{-1} s^{-1}
Cyclohexylamine	8.86	0.08	1,4-Piperazine	8.21	1.2
t-Butylamine	8.83	0.66	Diethylamine	8.01	1.9
Isopropylamine	8.72	0.05	Piperidine	7.85	0.92
Benzylamine	8.64	0.26	DABCO	7.52	7.3
Pyrrolidine	8.30	2.1	Triethylamine	7.50	9.3
Hexamethylenetetramine	8.26	0.20	*N*-Methylaniline	7.30	27
			NN-Dimethylaniline	7.10	120

The hypothesis that the $^1O_2$ quenching processes proceed via charge-transfer states was confirmed further in a study[40] of the quenching of $^1O_2$ and of the fluorescence of aromatic hydrocarbons by different amines, which takes place in an electronically excited charge-transfer complex formed by the aromatic compound and the amine. A linear correlation between the logarithm of the quenching rate constant and a quantity characterising the affinity of the excited singlet molecule for oxygen was demonstrated[40] for each amine investigated. It is of interest that the point characterising the rate constant for the quenching of singlet oxygen also fits on the straight line plotted for data on the quenching of the fluorescence of the singlet states of aromatic compounds.

2. Quenching via Energy Transfer

The quenching of $^1O_2$ via energy transfer proceeds in accordance with the equation

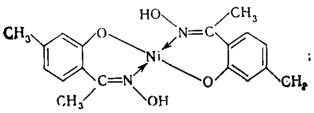
$$^1O_2 + {}^1Q_0 \rightarrow {}^3O_2 + {}^3Q_0, \tag{26}$$

where $^1Q_0$ and $^3Q_0$ are the ground singlet and triplet states of the quenching agent. This process does not require a change in the overall spin and is therefore allowed. The change in the multiplicity of the energy levels of oxygen alone is forbidden by Wigner's rule and its probability is therefore low. In order that reaction (26) should have a high rate constant, it is necessary that the condition $E^1O_2 \geqslant E^3Q_0$ holds for the energies of the corresponding states of oxygen and the quenching agent. Since E^1O_2 is only 22.6 kcal mole^{-1}, the energy of the triplet level of the effective quenching agent for $^1O_2$ must be very low.

The first investigation of a quenching agent operating via an energy transfer mechanism was carried out by Foote et al.,[11] who observed a very marked (20-fold) decrease of the rate of photosensitised oxidation of 2-methylpent-2-ene (0.1 M) in the presence of a β-carotene concentration smaller by a factor of 1000. The efficiency of this quenching agent surpasses all others which have been investigated. The quenching process results in the *cis–trans* isomerisation of β-carotene. It was known that β-carotene quenches the low-energy (29 kcal mole^{-1}) triplet state of chlorophyll with a diffusional rate constant, i.e. $E^3Q_0 \leqslant 29$ kcal mole^{-1}.[52] The efficiency of the quenching of $^1O_2$ decreases when β-carotene, which contains a system of 11 conjugated bonds, is replaced by other quenching agents of this class but with shorter conjugated chains. The compound with five conjugated bonds altogether failed to inhibit the oxidation reaction.

Although the energy of the triplet level of β-carotene was unknown, Foote et al.[11] concluded on the basis of these findings that the quenching of $^1O_2$ by β-carotene proceeds via an energy transfer mechanism with a diffusional rate constant. The value of k_q which they adopted is listed in Table 2. The constant k_d calculated from it for methanol proved to be 1×10^5 s^{-1}, which agrees very well with subsequent direct measurements (Table 1).

The quenching of $^1O_2$ by the transfer of the electronic excitation energy to β-carotene was demonstrated by a direct method in a study[25] where singlet oxygen, obtained by laser flash photolysis induced the formation of the triplet state of β-carotene, and the kinetics of its accumulation and destruction were investigated. The constant k_q was found to be close to the value obtained[11] on the hypothesis that the quenching proceeds in each encounter between $^1O_2$ and β-carotene. Other quenching agents with low triplet levels were discovered by Farmilo and Wilkinson[25], for example:



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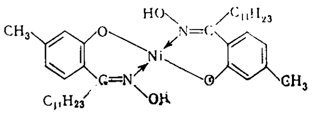

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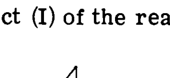
These quench $^1O_2$ with near diffusional rate constants—3.0×10^9 and 2.7×10^9 respectively. The quenching by these compounds apparently proceeds via the energy transfer mechanism. This can also be confirmed by the fact that, for example, the palladium complex having the same structure but with a higher triplet level quenches with a significantly lower rate constant (6×10^7).[25] Carlsson et al.[44] obtained $k_q > 10^9$ litre mole^{-1} s^{-1} (Table 5) for a number of organometallic compounds and at least some of them presumably function as energy acceptors. For less effective organometallic compounds, it has not so far been possible to establish any correlation between their geometry, properties, and ability to quench $^1O_2$.[22] However, in later investigations it was stated that diamagnetic nickel chelates quench $^1O_2$ and also the triplet state of ketones more effectively than the paramagnetic chelates[54]. It has been suggested[22] that the quenching mechanism may involve the formation of complexes of different kinds between the organometallic compounds and $^1O_2$.

IV. CHEMICAL REACTIONS OF QUENCHING AGENTS

The data presented above show that substances with low ionisation potentials, which are typically reducing agents, and substances with a low triplet level are able to quench singlet oxygen. Presumably the reducing agents react with singlet oxygen, since it is an oxidising agent and the excited states formed after energy transfer to the triplet levels of the quenching agents react with both $^1O_2$ and $^3O_2$. The literature data[12,16] showing that certain quenching agents, for example diazabicyclo[2,2,2]octane (DABCO), ethyldiisopropylamine, *NNNN′*-tetramethylethylenediamine, and allylamine in bromobenzene and thiophen and methanethiol in the gas phase do not react at all with $^1O_2$ should probably be understood as merely an indication that the rate constants for the chemical interactions of these compounds with $^1O_2$ are low in absolute magnitude and are much smaller than the quenching rate constants.

Apart from the reaction with $^1O_2$, in photosensitised oxidation processes the quenching agent may interact with the triplet state of the photosensitiser. The reaction of the quenching agent (with $^1O_2$ or ^3S) which becomes dominant under the given conditions depends on the nature of the photosensitiser, the quenching agent, the medium, and the concentrations of the quenching agent and oxygen.

The possible involvement of the triplet states of sensitisers in the photochemical oxidation reactions of quenching agents belonging to the class of amines has been examined most fully and proved by Batholomew and Davidson[55,56]. In the first of these investigations, a study was made of the composition of the product and the quantum yields of the absorption of oxygen and the formation of products in the oxidation of primary, secondary, and tertiary amines as well as *N*-alkylanilines photosensitised by benzophenone were measured. Aliphatic amines reacted with formation of carbonyl compounds (after the rupture of the C–N bond) and imines. *N*-Alkylanilines formed products resulting from the rupture of the C–N bond. The involvement of amines in the direct reaction with ^3S was demonstrated by measurements of the quantum yields Φ_{O_2} of the absorption of oxygen. The values of Φ_{O_2} for tertiary amines, for example triethylamine (0.1 M in benzene) and tribenzylamine (0.1 M in benzene), exceed unity, although these compounds are known to be powerful quenching agents for $^1O_2$. Additional confirmation was obtained by investigating the composition of the products. *In vacuo* and in the presence of oxygen, the dealkylation reaction characteristic of *N*-alkylanilines takes place and the same product (I) of the reaction of DABCO (II) is formed:



(I)
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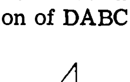

(II)
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In the second study[56], where the same reactions were investigated but dyes were employed as photosensitisers, the formation of the same products was observed, i.e. the dyes behave like benzophenone, which acts typically as a dehydrogenating agent. It was shown that the most readily oxidisable tertiary amines effectively decolorise the dye in the absence of oxygen and that the rate of photochemical oxidation increases with decrease of the concentration of oxygen. Both these findings support the involvement of amines in the direct reaction with ^3S.

Another mechanism, involving the direct interaction of amines with $^1O_2$, was examined and its validity was proved in other investigations[14,15]. The authors observed a new reaction of $^1O_2$—the formation of stable nitroxy-radicals in the sensitised oxidation of secondary and tertiary amines: homotropine, 1,1′- and 1,2′-diadamantylamines, 2,2,6,6-tetramethyl- and 1,2,2,6,6-pentamethyl-4-hydroxypiperidines, 4,4′-dimethoxy-, 4,4′-dicumenyl, and 4,4′-di-t-octyl-diphenylamine, and 2,7-di-t-octylphenothiazine. The oxidation was observed in liquid (8 : 1 benzene–ethanol mixture, concentration 10^{-3}–10^{-2} M) and solid [polystyrene, poly(methyl methacrylate), and polycarbonate] solutions irradiated with light corresponding to the absorption bands of the photosensitisers—Bengal Rose or Methylene Blue. The degree of conversion of amines in this process depends on the structure of the amine and the stability of the nitroxy-radicals and can reach several tenths. The involvement of $^1O_2$ in this reaction is confirmed by the lack of dependence of the measured rate constant for the formation of nitroxy-radicals on the oxygen concentration and the nature of the photosensitiser and also by the inhibition of the oxidation reaction by $^1O_2$ quenching agents, the efficiency of which may be calculated beforehand from the literature values of k_q.

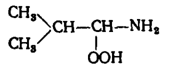
In most studies on the photosensitised oxidation of amines, the composition of the products and the rates and stoichiometries of the reactions are considered, but not the mechanisms of the primary photochemical processes. Below we shall therefore speak of the reactions of quenching agents in photosensitised oxidation processes without discussing specific mechanisms.

Table 9. The stoichiometry of the photosensitised oxidation of amines.

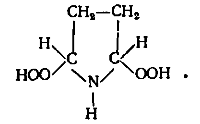
Amine	Absorption of O_2, moles per mole of substrate	References
Nicotine	1*	57
Methyl-, n-propyl-, isopropyl-, isobutyl-, and isopentyl-amines	1	13
Diethylamine, piperidine, pyrrolidine	2	13
Triethylamine	2.6	13
	3.06	28
t-Butylamine	No reaction	13

* Reaction in aqueous solution. The pyrrolidine component of the molecule is oxidised. In methanol three moles of O_2 are absorbed[32] instead of one.

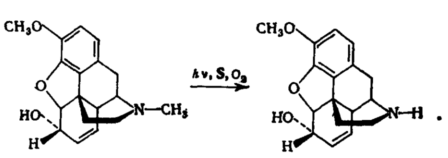
The data on the stoichiometry of the photosensitised amine oxidation reactions are presented in Table 9. According to Schenck[13], the formation of α-aminohydroperoxides corresponds to this stoichiometry, for example:



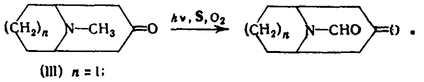
$$(CH_3)_2CH{-}CH(OOH){-}NH_2 ,$$



Accordingly, t-butylamine, which does not contain hydrogen atoms in the α-position, does not undergo photosensitised oxidation. However, as stated above, the photosensitised reactions can lead to other products—imines, carbonyl compounds, and products of the dealkylation of *N*-alkylamines[55,56]. Products of this type have been detected together with the formation of hydroperoxides in photosensitised oxidation reactions of primary, secondary, and tertiary n-butylamines.[57] Demethylation reactions have been observed in the photosensitised oxidation of steroid derivatives of the type $R{-}N(CH_3)_2$ (R = steroid residue)[58] and codeine[59]:



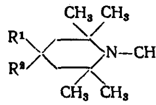
In the reactions of the alkaloids[60] pseudopelletierine (III) and tropinone (IV) and the steroid derivatives $R{-}N(CH_3)_2$,[58] the *N*-methyl groups were found to be oxidised to *N*-formyl groups, for example:



(III) *n* = 1;
(IV) *n* = 0

There are as yet no literature data concerning the ability of these compounds to quench $^1O_2$; they should probably behave as strong quenching agents, like other tertiary amines.

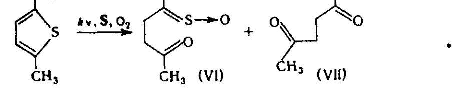
The absorption of oxygen by piperidine derivatives,



(V)

where $R^1 = R^2 = H$ or $R^1 = H$ and $R^2 = OH$, has been observed[41]. These compounds are probably oxidised fairly rapidly, since the rate of absorption of oxygen in the photochemical oxidation of 2-methylpent-2-ene (8×10^{-3} M), or 9,10-dimethoxyanthracene (8×10^{-3} M), or 9,10-dimethoxyanthracene (8×10^{-3} M) after the addition of compound (V) at a concentration of 5×10^{-2} M actually increases somewhat, although compounds (V) are known as quenching agents for $^1O_2$ (Table 4).

The absorption of oxygen and the formation of oxidation products were also observed in the presence of quenching agents of another class—sulphur-containing compounds. For example, analysis of the products of the oxidation of dimethyl and diethyl sulphides by singlet oxygen in the gas phase revealed the formation of sulphoxides[12]. The absorption of oxygen was observed in the photosensitised oxidation in methanol of disulphides related to cystine[61]. In the oxidation of 2,5-dimethylthiophen (0.01 M) photosensitised by Methylene Blue two main products were detected—the *cis*-sulphene (VI) and the *trans*-diketone (VII):



The ratio of the concentrations of (VI) and (VII) depends significantly on the solvent. In chloroform the yield of (VI) is 56% and that of (VII) 28%, while in Methanol the yields are 70% and 2% respectively.[62] The medium can have a significant influence not only on the composition of the product but also on the rate of oxidation. In this respect the influence of the medium is clearly manifested in the photochemical oxidation of β-carotene, which is

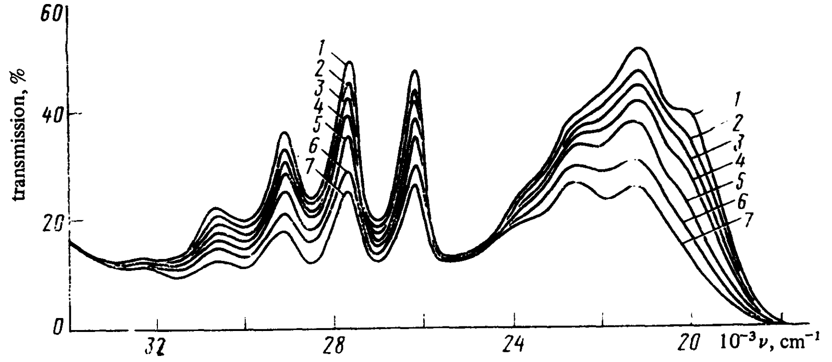


Figure 3. Changes in the absorption spectrum during the joint oxidation of anthracene (concentration 2.8×10^{-2} M) and β-carotene (concentration 0.67×10^{-2} M) in polystyrene; duration of irradiation (min): 1) 0; 2) 15; 3) 30; 4) 45; 5) 75; 6) 135; 7) 180.

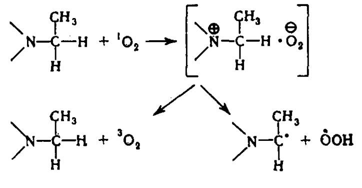
stable towards $^1O_2$ in solution but interacts readily with $^1O_2$ in a polymer matrix (polystyrene) with formation of an oxidation product, whose spectrum is illustrated in Fig. 3.[63]

Table 10. The ratios of the rates of physical and chemical quenching of singlet oxygen.

Quenching agent	Solvent	No. of $^1O_2$ quenching steps per reaction step	Refs.
β-Carotene	4:1 Benzene-methanol	>1000	11
β-Carotene	4:1 Benzene-methanol	<250	64
Diethyl sulphide	4:1 Benzene-methanol	20	11
NNN'N'-Tetramethyl-*p*-phenylenediamine	Methanol	>100	39
Diethyl sulphide	Gas phase	>40	12
Dimethyl sulphide	Gas phase	>16	12
Dimethyl disulphide	Gas phase	>1	12
Triethylene	Pyridine	9	28
Triethylamine	Gas phase	>100	28
Nicotine	Methanol	6	32
Mono-, di-, and tri-methylamines and mono-, di-, and tri-ethylamines	Gas phase	>100	51

The ratios of the rates for "physical" and "chemical" quenching presented in Table 10 show that the number of quenching steps per reaction step depends both on the properties of the quenching agent and on the medium in which the interaction takes place.

The mechanism of the effect of the solvent has not in essence yet been investigated. The hypothesis put forward by Smith[28] explains the tenfold increase of the rate constant for the chemical interaction of $^1O_2$ with triethylamine on passing from the gas phase to a pyridine solution by the increase of the lifetime of the triethylamine radical-cation in the polar solvent:



Very few rate constants for the chemical interaction of $^1O_2$ with quenching agents are as yet available. They are listed in Table 11.

Table 11. The rate constants for the chemical interaction of quenching agents with singlet oxygen.

Quenching agent	Solvent	k_r, litre mole^{-1} s^{-1}	Refs.
Dimethyl sulphide	Gas phase	1×10^4	12
Diethyl sulphide	Gas phase	1×10^4	12
Dimethyl disulphide	Gas phase	1×10^4	12
Diethyl sulphide	4:1 Benzene-methanol	3×10^5	11
Nicotine	Methanol	2×10^5	32
Triethylamine	Pyridine	1×10^6	28
4-Hydroxy-2,2,6,6-tetramethylpiperidine	8:1 Benzene-methanol	2.9×10^3*	15
4-Hydroxy-1,2,2,6,6-pentamethylpiperidine	8:1 Benzene-ethanol	2.3×10^3*	15
Di-(4-t-octylphenyl)-amine	8:1 Benzene-ethanol	2.6×10^4*	15

* The rate constant for the formation of the nitroxy-radical.

V. TRENDS IN FUTURE RESEARCH

1. Quenching Agents Acting via a Charge-Transfer Mechanism

The most effective of the quenching agents investigated, acting via a charge-transfer mechanism, have reaction rate constants of about 5×10^8 litre mole^{-1} s^{-1}. There is no doubt that compounds with maximum possible efficiency, quenching $^1O_2$ in each encounter, can be obtained within the framework of this mechanism by introducing more powerful electron-donating substituents. However, it is so far difficult to answer the question whether such quenching agents would be suitable for practical use. Unduly strong reducing agents may prove to be unstable towards oxidation by oxygen in the ground state. Furthermore, the interaction of $^1O_2$ with an unduly strong reducing agent may lead to the formation of free radicals and hence to a radical-chain reaction of the substrate. Effects of this kind have been observed, for example, in a study[65] where, in an oxidation reaction photosensitised by thionine, a transition was observed to a radical mechanism after a change of substrate—from 9,10-dimethylanthracene and tetramethylethylene, which are weak reducing agents, to thiourea, which is a much stronger reducing agent. Finally, in order to be able to predict the suitability of quenching agents with maximum efficiency for practical employment, it is necessary to know the resulting ratio k_r/k_q, i.e. whether or not such quenching agents would react too rapidly with $^1O_2$. In order to be able to answer this question, one must investigate the dependence of k_r/k_q on the ionisation potentials or σ constants of the substituents in the quenching agents.

2. Quenching Agents Acting via the Energy Transfer Mechanism

It is evident from the foregoing that several very effective quenching agents, acting via the energy transfer mechanisms and deactivating $^1O_2$ in each encounter, are now known. The energy transfer from $^1O_2$ to an electronic level of the quenching agent probably takes place only on direct contact between the electron shells of $^1O_2$ and the energy acceptor. Transfer over large distances, for example via an inductive-resonance mechanism, is hardly possible, since the probability of a radiative transition of $^1O_2$ to the ground state is very low. One must therefore assume that the practical limit of the efficiency of the quenching agent has already been reached. Of the two types of quenching agents—compounds with a system of conjugated bonds and complexes—the latter are preferable, since the class of complexes is much larger and within its limits there is a much greater scope for obtaining stable quenching agents with the required properties. β-Carotene and compounds having similar structures are very reactive in relation to free radicals and are readily oxidised by molecular oxygen ($^3O_2$). There is therefore little prospect for their employment as quenching agents, although in plant organisms one of the functions of carotenoids is the quenching of $^1O_2$.[64]

One cannot rule out the possibility that carbon black, which contains structures with fairly long chains of conjugated bonds, can act similarly to β-carotene.

3. Quenching in Polymer Matrices and the Role of Singlet Oxygen in the Photochemical Oxidation Reactions of Polymers

It follows from the only investigation[36] which has so far been carried out that the efficiencies of quenching agents in a solid matrix (polystyrene) are to a large extent equalised. On the basis of general considerations, this effect is presumably related to the limitation of the diffusional mobility of oxygen and of molecular motion in the matrix, which hinders the formation of the activated complex. This is confirmed by data[36] showing that sharp changes in the kinetic constants occur in the region of the glass temperature (T_g). In order to elucidate the mechanism of this phenomenon, systematic studies on various polymers above and below T_g, combined with measurements of the diffusion coefficients of oxygen and of the characteristics of molecular mobility, are now required.

As far as one can judge from the available data[36], the efficiencies of quenching agents in polymers at $T < T_g$ differ comparatively little and therefore in selecting quenching agents one should be guided more by their stability during processing and under the conditions obtaining in the employment of polymers, their solubility in and compatibility with the polymer, their low volatility, etc. rather than by their efficiency in the liquid phase.

In the measurements of the efficiencies of quenching agents both in solution and in the solid phase, it is desirable to employ the formation of nitroxy-radicals during the oxidation of secondary or tertiary amines by singlet oxygen as the indicator reaction[15]. The ESR method is highly sensitive. It is therefore possible to measure the influence of quenching agents on the rate of accumulation of radicals under the conditions of an almost constant concentration of the indicator substance. Furthermore, measurement of the rate by ESR obviates the need to determine the rate from absorption spectra, which is sometimes difficult.

The possible involvement of $^1O_2$ in the photochemical oxidations of polymers began to be discussed in the literature in recent years[43,44,66-74]. Depending on the type of polymer, two mechanisms are considered. The first mechanism, which obtains in polymers containing double bonds, involves the direct interaction of $^1O_2$ with the macromolecule. The second mechanism, which applies to polymers without double bonds, presupposes the interaction of $^1O_2$ with the unsaturated compounds formed as a result of the photochemical process. In both mechanisms, the effect of $^1O_2$ reduces to the acceleration of the accumulation of hydroperoxides giving rise to photochemical branching. Processes involving the quenching by oxygen of the triplet states of carbonyl or aromatic compounds, which may be present as impurities or can form part of the composition of the macromolecules, are considered as sources of $^1O_2$.

Neither the first nor the second mechanisms has yet been proved. Very convincing experiments on certain polymers (for example polymers containing double bonds) established the possibility of their oxidation by the singlet oxygen generated chemically, or photochemically, or in an electric discharge. However the possibility, in principle, of the involvement of $^1O_2$ in the oxidation process does not by itself imply that the $^1O_2$ reactions really make any considerable contribution to the photochemical oxidation of polymers with double bonds in the absence of artificially created sources of $^1O_2$.

The difficulty of proving this mechanism consists in the fact that $^1O_2$ does not oxidise directly polymers without electron-accepting groups (unsaturated, condensed aromatic, etc.). The effect of $^1O_2$ must therefore be investigated not by itself but against the background of the photochemical reaction of the polymer, which generates groups capable of accepting $^1O_2$.

We believe that the problem of the involvement of $^1O_2$ in photochemical oxidation reactions of polymers can be usefully solved in two stages. The first stage involves the study of the possibility, in principle, of the acceleration of the photochemical oxidation of the given polymer with the aid of an artificial source of $^1O_2$. When a photosensitiser dye is used as the source of $^1O_2$, one can suggest for the elucidation of the possible involvement of $^1O_2$ experiments with two light sources—a short-wavelength source whose light is absorbed by the polymer or the photosensitising mixture and a long-wavelength source whose light is absorbed only by the dye. After appropriate control experiments with both sources, the acceleration of the photochemical reaction of the polymer with periodic or permanent inclusion of the additional long-wavelength source could probably be regarded as proof of the involvement of singlet oxygen.

In the second stage of the investigation it is necessary to measure the power of the internal source of singlet oxygen. A conclusion concerning the role of oxidation by singlet oxygen can probably be arrived at by comparing the power of the internal source with that of an external source sufficient for an appreciable acceleration of the photochemical process.

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Polarographic Study of Aminoalkyl Esters of $\alpha\beta$-Unsaturated Acids and Their Reactions

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The review is devoted to the polarographic study of the reactions of aminoalkyl esters of $\alpha\beta$-unsaturated acids: electrochemical reduction, hydrolysis (including hydrolysis in a two-phase system), partition, and isomerisation. Detailed polarographic characteristics and equations for the polarographic wave and the kinetics and equilibria of the reactions using the limiting polarographic current are presented. The corresponding analytical applications of the method are considered. The kinetics and mechanisms of the processes are discussed from the standpoint of the structure of the electrical double layer, the acid-base properties of the aminoalkyl esters, and intramolecular hydrogen bonds in conjunction with correlation analysis. A comparison is made with data obtained by pH-stat and spectrophotometric methods. The bibliography includes 166 references.

CONTENTS

I. INTRODUCTION

Interest in aminoalkyl esters of $\alpha\beta$-unsaturated acids has been aroused comparatively recently and for this reason we shall consider briefly the problems concerning the applications of these esters and also the methods for their synthesis.

Aminoalkyl methacrylates and acrylates, monomers with functional groups, are used in the manufacture of a wide variety of polymeric materials: synthetic rubbers[1], rubber suitable for the manufacture of tyres[2], latexes[3], vulcanising agents for rubbers[4-9], fibreglass[10-18], anionic polyelectrolytes and polyampholytes[19-25], coatings[26-33], modified cellulose materials[34-37], and physiologically active polymers[38-42]. Certain other applications of the esters have also been described[43-53].

The following methods are used to synthesise esters of methacrylic and acylic acids containing in the alkoxy-radical a tertiary amino-group or a secondary amino-group with a t-alkyl or aryl substituent at the nitrogen atom[51-53]. (1) Esterification of aminoalcohols by unsaturated acids. The use of this method is limited owing to the necessity to remove from the required monomers an admixture of the salt of the initial acid and the aminoalcohol and also owing to the inadequate yields of the monomers. (2) Acylation of aminoalcohols by acid chlorides. The latter method is more universal and makes it possible to obtain high yields of the methacrylate and acrylate derived from a wide variety of aminoalcohols. However, owing to the low availability and high cost of acid chlorides, the applications of this method are as a rule limited to preparative laboratory syntheses. (3) Transesterification of lower unsaturated acid esters with aminoalcohols. Because of the low cost of the initial methacrylate and acrylate esters, their high purity and stability, and also the comparatively simple technology and high yields of the required monomers, this method is most widely used in practice. Alkaline metal, alkaline earth metal, and titanium alkoxides are used as effective process catalysts.

Methacrylates and acrylates containing in the alkoxy-group a primary amino-group or a secondary amino-group with unbranched or only slightly branched alkyl residues at the nitrogen atom are as a rule obtained in the form of hydrochlorides by the interaction of acid chlorides with aminoalcohol hydrochlorides.

The aminoalkyl methacrylate and acrylate esters discussed in this review were obtained mainly by transesterification (method 3) and from acid chlorides.

In connection with the expanding use of aminoalkyl esters of $\alpha\beta$-unsaturated acids, studies of the physicochemical properties of these compounds and the development of highly sensitive physicochemical methods for their determination are assuming increasing importance. This review is devoted to this problem and is concerned mainly with results obtained by the polarographic method: polarographic studies of the hydrolysis, isomerisation, and partition reactions and polarographic methods for the determination of the aminoalkyl esters. A number of important advantages of the polarographic method for the investigation of the kinetics and equilibria of the above reactions are noteworthy: (1) the possibility of recording kinetic curves without sampling; (2) the comparatively simple solution of the problem of the maintenance of a constant pH and ionic strength owing to the high sensitivity of the method, etc.

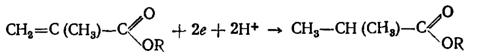
Since the polarographic method yields at the same time valuable information about the mechanism of the electrochemical reduction of the test compounds, these data have also been included in the review. Compared with methacrylate and acrylate esters without an amino-group in the alkoxy-moiety, the corresponding aminoalkyl esters are of considerable interest as regards their electrochemical behaviour, since, depending on the pH of the solution, they can exist in both protonated and non-protonated states. This factor makes it possible to investigate the intramolecular catalysis in the hydrolysis of the aminoalkyl esters as a function of the pH.

II. POLAROGRAPHIC CHARACTERISTICS AND THE MECHANISM OF ELECTROCHEMICAL REDUCTION

For comparison, we shall consider in this section also certain data referring to unsaturated acid esters without an amino-group in the alkoxy-moiety.

The possibility of the polarographic reduction of esters with $\alpha\beta$-conjugated double bonds (the carbonyl and ethylene bonds) was demonstrated for the first time in relation to methyl methacrylate[54]. The reduction wave of methyl methacrylate ($E_{1/2} = -1.92$ V; here and henceforth the potentials are quoted relative to the normal calomel electrode) was obtained in the presence of lithium chloride or tetramethylammonium iodide in 25% ethanol as the supporting electrolyte.

Data have been published[55-62] on the reduction of methacrylates without an amino-group in the alkoxy-moiety using non-aqueous and mixed solvents. The polarographic behaviour of methacrylates with substituents other than amino-groups in the alkoxy-moieties has been discussed[63,64]. The reduction involves the ethylene bond with formation of isobutyrate esters[55-57]:



$$CH_2{=}C(CH_3){-}C\begin{smallmatrix}\nearrow O\\ \searrow OR\end{smallmatrix} + 2e + 2H^+ \rightarrow CH_3{-}CH(CH_3){-}C\begin{smallmatrix}\nearrow O\\ \searrow OR\end{smallmatrix} \quad (1)$$

The reduction of methacrylates and acrylates containing an alkylamino-group has been studied[65-72] in both aqueous buffer solutions[65-67,71] and using non-aqueous solvents (alcohol, dimethylformamide[68-70]). The polarographic characteristics of acrylate and methacrylate esters in various supporting electrolytes are presented in Tables 1 and 2. To facilitate the comparison, the limiting current constant I_{lim} is defined as the limiting current divided by the characteristic of the capillary; the dimensions of I_{lim} are μA litre mole^{-1} mg$^{-2/3}$ s$^{1/2}$. The limiting current constant undivided by the capillary characteristic is denoted henceforth by K_{lim}.

The reduction of aminoalkyl methacrylates is irreversible like that of methacrylates containing alkoxy-moieties without an amino-group[63]; the slopes of the $E - \lg[\bar{i}/(\bar{i}_d - \bar{i})]$ straight lines is 75–85 mV for neutral buffer solutions and 60–67 mV for alkaline solutions[66,71].

In studies on the reduction of a number of aminoalkyl acrylates and methacrylates in dimethylformamide it was noted[70] that the limiting current constant is smaller approximately by a factor of two than in a protic solvent. However, the addition of proton donors (water, phenol, propargyl alcohol) to dimethylformamide leads to an increase of the limiting current to values approximately equal to those in a protic solvent (Table 1). In consequence of the differences between the properties of the free radicals formed in the first stage of the reduction of monomers, under these conditions the limiting current for the methacrylates reaches constant values at much lower concentrations of proton donors than for acrylates (see below)[57]. The increase of the limiting current in the presence of proton donors has been explained[70] by the fact that in non-aqueous dimethylformamide the process stops at the stage involving the formation of radical-anions,

$$CH_2{=}C(CH_3)COOR + e \rightarrow \dot{C}H_2{-}\bar{C}(CH_3)COOR, \quad (2)$$

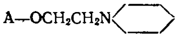
which probably dimerise subsequently. The one-electron mechanism of the reduction of methacrylates in an aprotic medium (dimethylformamide) has been confirmed[62] for methyl methacrylate.

In the presence of proton donors, the radical-anion is protonated[70]:

$$\dot{C}H_2{-}\bar{C}(CH_3)COOR + HA \rightarrow \dot{C}H_2{-}CH(CH_3)COOR \quad (3)$$

which facilitates subsequent reduction. Calculation of the number of electrons involved in the reaction by the Il'kovich equation using the diffusion coefficients for compounds of a similar type showed that the reduction process involves the addition of two electrons[58,65,69]. However, in the case of the dimethacrylate derived from triethylene glycol the limiting currents in both anhydrous dimethylformamide and in the presence of proton donors are almost the same[74], which indicates the absence of the radical-anion protonation stage. This finding has been explained[74] by the possible amination of the radical-anion (or the dimeric biradical) by the tetraalkylammonium cations from the supporting electrolyte.

Table 1. The polarographic characteristics of the reduction of acrylate and methacrylate esters [$A{=}CH_2{=}CHC\begin{smallmatrix}\nearrow O\\ \searrow\end{smallmatrix}$; $M{=}CH_2{=}C(CH_3)C\begin{smallmatrix}\nearrow O\\ \searrow\end{smallmatrix}$; 25°C].

Compound	0.05 M $(C_2H_5)_4NI$ in dimethylformamide					0.05 M $(C_2H_5)_4NI$ in CH_3OH		
	$-E_{1/2}$, V	I_{lim}			References	$-E_{1/2}$, V	I_{lim}	References
		DMF	1 M (DMF + H_2O)	8 M (DMF+phenol)				
$A{-}OCH_2CH_2N(CH_2{-}CH{=}CH_2)_2$	2.081	2.17	2.34	4.46	70	—	—	—
$M{-}OCH_2CH_2N(CH_2{-}CH{=}CH_2)_2$	2.253	2.07	3.45	4.08	70	—	—	—
$A{-}OCH_2CH_2N(C_2H_5)_2$	2.118	—	2.16	4.34	70	—	—	—
$M{-}OCH_2CH_2N(C_2H_5)_2$	2.269	—	3.84	4.70	70	2.07	5.60	69
	2.087	1.47	—	—	57	—	—	—
	2.260	3.91	—	—	57	2.04	5.56	69
$A{-}OCH_3$	—	—	—	—	—	1.83*	3.23*	56
$M{-}OCH_3$	—	—	—	—	—	1.92*	2.60*	56
$M{-}OC_2H_5$	—	—	—	—	—	1.94**	2.53**	56
$M{-}OCH_2{-}CH{=}CH_2$	—	—	—	—	—	1.97*	2.75**	56
$A{-}OC_4H_9$	2.111	—	1.77	5.00	70	—	—	—
$M{-}OC_4H_9$	2.252	—	3.50	5.50	70	2.02**	2.08**	56

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* In 0.02 M $(C_2H_5)_4NI$.

** In 0.1 M Li_2SO_4; 10% CH_3OH.

Table 2. The polarographic characteristics of the reduction of methacrylate esters $[M{=}CH_2{=}C(CH_3)C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown}$; 25°C; aqueous solution]

No.	Compound	pK_a^*	pH 7.40, universal buffer (Li$^+$), ionic strength 0.05			pH ~ 12 (LiOH); ionic strength 0.02		
			$-E_{1/2}$, V	I_{lim}	References	$-E_{1/2}$, V	I_{lim}^{**}	References
1	$M{-}OCH_2CH_2N(CH_2CH{=}CH_2)_2$	6.93	—	—	—	1.976	—	65
2	$M{-}OCH_2CH_2N(CH_3)CH_2CH{=}CH_2$	7.39	—	—	—	1.956	2.35	65
3	$M{-}OCH_2CH_2N(CH_3)_2$	7.94	1.666	3.60	65	1.934	2.87	65
4	$M{-}OCH(CH_3)CH_2N(CH_3)_2$	7.96	1.678	3.46	65		—	65
5	$M{-}OCH_2CH_2N(CH_3)C_4H_9$	8.28	1.632	3.43	65	1.926	2.35	65
6	$M{-}OCH(CH_3)CH_2N(C_2H_5)_2$	8.65	1.645	3.35	65			
7	$M{-}OCH_2CH_2N(C_2H_5)_2$	8.66	1.645	3.50	65	1.912	2.76	65
8	$M{-}OCH_2CH_2N(C_3H_7\text{-iso})_2$	8.77	1.713	3.30	65			
9	$M{-}OCH_2CH_2NHC(CH_3)_3$	9.12	1.775	3.20	65	1.898	2.68	65
10	$M{-}OCH_2CH_2C{\equiv}N$	—	—	—	—	1.885	2.62	63
11	$M{-}OCH_2C{\equiv}CH$	—	—	—	—	1.908	2.62	63
12	$M{-}OCH_2CH_2N^+(CH_3)_3$	—	—	—	—	1.743	—	63
13	$M{-}OCH_2CH_2Cl$	—	—	—	—	1.930	2.78	63
14	$M{-}OCH_2C_6H_5$	—	—	—	—	1.951	2.89	63
15	$M{-}OCH_2CH_2OCH_3$	—	—	—	—	1.963	2.62	63
16	$M{-}OCH_2CH_2OC_2H_5$	—	—	—	—	1.963	2.62	63
17	$M{-}OCH_3$	—	—	—	—	1.968	2.76	63
18	$M{-}OC_2H_5$	—	—	—	—	1.973	2.62	63
19	$M{-}OC_4H_9$	—	—	—	—	1.993	2.70	63

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* K_a are the acid dissociation constants of the aminoesters taken from the literature[72,73].

** The currents I_{lim} in the alkaline pH range were found by extrapolation to zero time[71].

The protonation of the radical-anion observed in the presence of proton donors is evidently very rapid, since the values of $E_{1/2}$ and K_{lim} for methacrylates and acrylates without an amino-group in the molecules are independent of the pH (pH 7.5–12.5).[57]

The limiting current for the reduction of aminoalkyl methacrylates in an aqueous buffer solution at a pH close to that of the neutral medium is diffusional[65,71] (the slope of the $\lg i_{lim} - \lg H_{Hg}$ straight lines is 0.5; temperature coefficient 0.95–1.37% per degree), as for methacrylates without an amino-group in the alkoxy-moiety[63]. The values of $E_{1/2}$ and K_{lim} in the range pH < 8.5–9.5 are almost independent of the pH; $E_{1/2}$ is also independent of the concentration of the aminoalkyl ester and $\bar{i}_{lim}$ is directly proportional to its concentration.

In the alkaline pH range (pH > 8.5–9.5), the reduction process has a kinetic mechanism[66] (the slope of the $\lg \bar{i}_{lim} - \lg H_{Hg}$ straight lines is 0.26–0.39; temperature coefficient 2.5–3.9% per degree), which may in fact explain the decrease of the limiting current constant (Table 2). The kinetic mechanism of the reduction process in alkaline solution has been accounted for[66] by the influence on this reaction of the protonation of the neutral aminoalkyl ester molecule (at the nitrogen atom) preceding the electrochemical stage proper. The limiting current for the analogous esters without an amino-group remains diffusional also in the alkaline pH range[63]. The protonation of aminoalkyl esters proceeds in a very thin reaction layer at the surface of the electrode[66]. Under these conditions, the main proton donors are hydronium ions; on the other hand, with increase of pH and the acid dissociation constant of the aminoalkyl ester (K_a), water molecules may also be involved in the protonation stage[66]. In the region of kinetic waves, K_{lim} decreases with increasing pH and $E_{1/2}$ shifts towards negative values.

The following mechanism of the above electrode process has been proposed[66]:

$$\begin{tikzcd}
{} & RN \arrow[l, "e", "(III)"'] \arrow[r, shift left, "\overset{(I)}{H^+}"] & RNH^+ \arrow[l, shift left] \arrow[r, "e", "(II)"'] & {} \\
 & RN \arrow[u, "\text{diff.}"'] \arrow[r, shift left] & RNH^+ \arrow[l, shift left] \arrow[u, "\text{diff.}"']
\end{tikzcd}, \qquad (4)$$

including the occurrence in the general case of simultaneous reactions involving the reduction of the non-protonated (RN) and protonated (at the nitrogen atom; RNH$^+$) forms of aminoalkyl esters. In the region of the rise in the wave, there is then also electrochemical inhibition (the process is irreversible) in both simultaneous electron transfer stages.

Like methacrylates without an amino-group[63,75] and aminoalkyl esters of other acids[76], aminoalkyl methacrylates[66,71] are adsorbed on the mercury electrode[66,71]; however, at potentials more positive by 0.4–0.5 V than the half-wave potential, they are desorbed[66]. Bearing in mind the high negative reduction potential of aminoalkyl methacrylates, the influence of their adsorption on the chemical electrode reactions can probably be neglected.

In alkaline solutions (pH ⩾ pK_a) the simultaneous reduction reactions (II) and (III) take place [mechanism (4)]. If only reactions (I) and (II) occur (slow protonation), they are described by the kinetic equation[77]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-3} n \bar{S} F k^0_{el}}{K_{lim}} + \Psi_1 \left(\frac{\alpha n_a - 1}{\alpha n_a} \right) + \frac{RT}{\alpha n_a F} \ln \frac{[H^+]}{K_a} + \frac{RT}{\alpha n_a F} \ln \frac{\bar{i}_d}{\bar{i}_{lim}}, \qquad (5)$$

where α is the transfer coefficient, n_a the number of electrons involved in the potential-determining reaction, $\bar{S}$ the surface area of the mercury drop (in cm^2), k^0_{el} the rate constant for the electrochemical stage (in cm s^{-1}) and Ψ_1 the potential in the outer Helmholtz plane.

When only reaction (III) takes place [mechanism (4)], $E_{1/2}$ is given by the equation[78]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{10^{-8} n\bar{S}Fk^0_{\mathrm{el}}}{K_{\mathrm{lim}}} + \Psi_1. \tag{6}$$

It follows from Eqns. (5) and (6) that in alkaline solutions (αn_a = 0.8–0.9) in the presence of Li^+(LiOH) the relative influence of reactions (I) and (II) will be greater than in a solution at the same pH but in the presence of the $(Alk)_4N^+$ cation (the Ψ_1 potential is more negative in the case of Li^+).[79] The observed shift of $E_{1/2}$ towards negative values (Fig. 1) with increase of K_a in 0.02 M LiOH solution has therefore been explained[66] by the dominant influence on $E_{1/2}$ of the term of Eqn. (5) containing K_a.

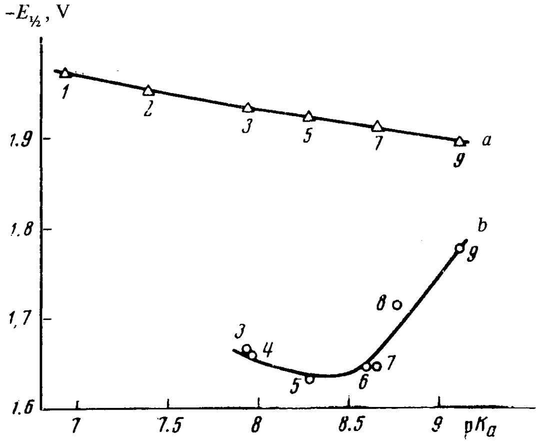

Figure 1. Variation of $E_{1/2}$ with the acid dissociation constants of aminoalkyl esters[66]: *a*) 0.02 M LiOH; *b*) universal buffer solution with LiOH + 0.03 M LiCl (pH 7.4; ionic strength 0.05). The numbers against the symbols correspond to the numbers of the esters in Table 2.

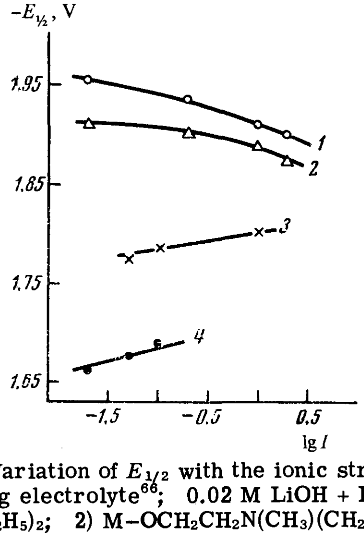

Figure 2. Variation of $E_{1/2}$ with the ionic strength *I* of the supporting electrolyte[66]; 0.02 M LiOH + LiCl; 1) $M{-}OCH_2CH_2N(C_2H_5)_2$; 2) $M{-}OCH_2CH_2N(CH_3)(CH_2{=}CH{-}CH_2)$; universal buffer solution with LiOH + LiCl (pH 7.4); 3) $M{-}OCH_2CH_2NHC(CH_3)_3$; 4) $M{-}OCH_2CH_2N(CH_3)_2$ ($M = CH_2{=}C(CH_3)C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow}$ throughout).

An increase of the ionic strength of an alkaline solution (pH 12) leads[66] to a shift of $E_{1/2}$ towards less negative values (Fig. 2), as for esters with other uncharged alkoxy-groups[63]. The replacement of Li^+ by $(Alk)_4N^+$ in these solutions also greatly facilitates the reduction of the aminoalkyl esters (Fig. 3). The observed phenomena have been explained[66] by the increasing influence of reaction (III) [mechanism (4)] as a result of its acceleration due to the decrease of the absolute value of the Ψ_1 potential[79]. According to Eqn. (6), the change in the rate constant for the electrochemical stage k^0_{el} in solutions with $(Alk)_4N^+$ assumes a considerable importance.

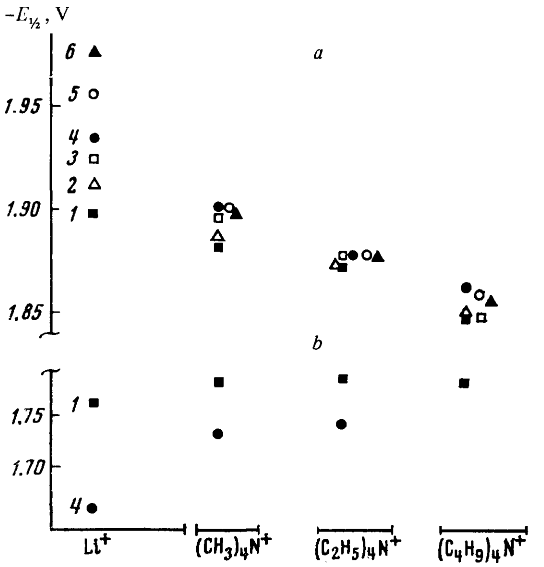

Figure 3. Variation of $E_{1/2}$ with the nature of the cation (Kt^+) of the supporting electrolyte[66]: *a*) 0.02 M KtOH; *b*) universal buffer solution with the corresponding KtOH (pH 7.4; ionic strength 0.02): 1) $M{-}OCH_2CH_2NHC(CH_3)_3$; 2) $M{-}OCH_2CH_2N(C_2H_5)_2$; 3) $M{-}OCH_2CH_2N(CH_3)C_4H_9$; 4) $M{-}OCH_2CH_2N(CH_3)_2$; 5) $M{-}OCH_2CH_2N(CH_3)CH_2{-}CH{=}CH_2$; 6) $M{-}OCH_2CH_2N(CH_2{-}CH{=}CH_2)_2$.

As in the case of methacrylates without an amino-group[64], the values of $E_{1/2}$ for aminoalkyl esters in a non-protonated form are displaced towards less negative values with increase in the size of the cation of the indifferent electrolyte (Fig. 3):

$$\underrightarrow{Li^+;\ (CH_3)_4N^+;\ (C_2H_5)_4N^+;\ (C_4H_9)_4N^+.}$$

This is qualitatively consistent with the corresponding shift of the Ψ_1 potential[80,81] but the displacement of $E_{1/2}$ exceeds the value expected as a result of the Ψ_1-effect[82] and depends to a considerable degree on the size of the substituent in the ester molecule. This has been explained[64] on the basis of the concept[79,83] of specific interactions of the organic depolariser in tetraalkylammonium salt solutions where the electrolyte cation is adsorbed (this leads to the formation of a cationic complex in the adsorption layer). As a result of this interaction, the depolariser is "drawn into" the double layer by the strongly adsorbed tetraalkylammonium cation, which leads to an additional acceleration of the electrode process and a positive shift of $E_{1/2}$.

When the pH approaches the value of pK_a, reactions (I) and (II) predominate [mechanism (4)] for partly protonated aminoalkyl esters, and, taking into account the quasidiffusional wave, $E_{1/2}$ is expressed by the following equation under these conditions[84]:

$$E_{1/2}=\frac{RT}{\alpha n_a F}\ln\frac{10^{-8}n\bar{S}Fk^0_{\mathrm{el}}}{K_{\mathrm{lim}}}+\Psi_1\left(\frac{\alpha n_a-1}{\alpha n_a}\right)+\frac{RT}{\alpha n_a F}\ln\frac{[\mathrm{H}^+]}{K_a+[\mathrm{H}^+]}\,. \tag{7}$$

It follows from Eqn. (7) that, when the nature of the aminoalkyl ester changes, $E_{1/2}$ begins to experience the opposite influence of K_a in addition to the influence of k^0_{el}. As a result of this, the plot of $-E_{1/2}$ against pK_a passes through a minimum[66] (Fig. 1).

For fully protonated aminoalkyl esters (pH ≪ pK_a), $E_{1/2}$ corresponding to the diffusional wave is described by the following equation[78] [reaction (II) in mechanism (4)]:

$$E_{1/2}=\frac{RT}{\alpha n_a F}\ln\frac{10^{-8}n\bar{S}Fk^0_{\mathrm{el}}}{K_{\mathrm{lim}}}+\Psi_1\left(\frac{\alpha n_a-1}{\alpha n_a}\right). \tag{8}$$

In this pH range, the half-wave potential $E_{1/2}$ virtually ceases to depend on the pH of the solution[66] (Fig. 4). The considerable positive shift of $E_{1/2}$ with decrease of pK_a (pH 7.4) (Fig. 1) can be explained by the polarising influence of the substituents in the protonated aminoalkyl esters, which becomes enhanced owing to the intramolecular hydrogen bond (see below).

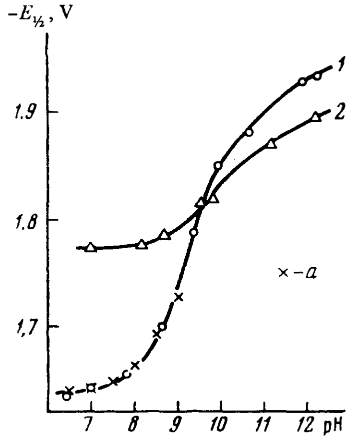

Figure 4. Variation of $E_{1/2}$ with pH of the universal buffer solution (LiOH) [66] [ionic strength 0.02 (+LiCl)]: 1) $M-OCH_2CH_2N(C_2H_5)_2$ (pK_a = 7.94); 2) $M-OCH_2CH_2.NHC(CH_3)_3$ (pK_a = 9.12); *a*) points calculated by Eqn. (7).

When Li^+ is replaced by $(Alk)_4N^+$ in the indifferent electrolyte in neutral buffer solutions at pH 7.4 (in contrast to alkaline solutions at a pH 12), $E_{1/2}$ for the aminoalkyl esters shifts towards negative values (Fig. 3),[66] which is consistent with Eqns. (7) and (8) (αn_a = 0.7–0.8). A similar influence of the indifferent electrolyte has been observed for an aminoalkyl ester with a quaternary nitrogen atom [$-CH_2CH_2N^+(CH_3)_3$], which is also consistent with the theory[80]. $E_{1/2}$ for protonated aminoalkyl esters[66] and the ester with a quaternary nitrogen atom[63] shifts in the same direction with increasing ionic strength [Eqns. (7) and (8)].

A tendency towards a negative shift of $E_{1/2}$ with increase of the molecular weight of methacrylates (methyl, ethyl, and butyl methacrylates) as been noted[61], which the authors explained by the positive inductive effects of the alkyl group, increasing from the methyl to the butyl group. This leads to an increase of electron density at the vinyl bond and hinders its reduction. This question has been examined qualitatively[63] on the basis of the correlation equation[85]

$$\Delta E_{1/2}=\rho^*_\pi\sigma^*_R, \tag{9}$$

where ρ^*_π is the constant defining the sensitivity of $E_{1/2}$ for the given group of compounds to the influence of the solvent and σ^*_R is the Taft constant. A satisfactory correlation has been obtained in the range of values of σ^*_R from −0.13 to 0.8, characterised by the following parameters: $\rho^*_\pi = 0.114 \pm 0.008$; $S = \pm 0.007$; $r = 0.977$. Since the ester with a non-protonated amino-group does not deviate from the general correlation, this permitted the conclusion[63] that the inductive effect of the non-protonated amino group has a dominant influence on the electrochemical activity of the aminoalkyl esters and made it possible to explain the small experimental negative shift[69,86] of $E_{1/2}$ following the introduction of an alkylamino-group into the alkoxy-moiety of acrylates and methacrylates.

$E_{1/2}$ for the ester derived from β-trimethylammoniumethanol was found to deviate[63] from the $E_{1/2}$–σ^*_R linear relation, which was explained by the electrostatic effect of the field.

It is interesting to note that, in an alkaline solution (pH 12), $E_{1/2}$ for the aminoalkyl esters is also satisfactorily correlated with the $\sigma^*_{R_i}$ constants of the substituents at the nitrogen atom in the alkylamino-group ($\rho^*_\pi = -0.110 \pm 0.006$; $S = \pm 0.002$; $r = 0.995$).[71] However, under these conditions ρ^*_π is negative, suggesting the dominant influence in this series of the nitrogen protonation stage, which is accelerated with increasing positive inductive effect of the alkyl substituent at the nitrogen atom.

It has been noted[57] that, on passing from acrylate esters to the corresponding methacrylate esters, $E_{1/2}$ for the esters shifts by 0.1–0.15 V towards more negative values owing to the positive inductive effect of the α-methyl group (Table 1).

III. THE KINETICS AND MECHANISM OF HYDROLYSIS

1. Kinetic Characteristics

The kinetics of the hydrolysis of the aminoalkyl esters of acids containing tertiary and certain secondary amino-groups in the alkoxy-moiety have been studied. The presence of a primary amino-group and in many cases also of a secondary amino-group leads predominantly to the O–N migration of the acyl group (see below).

Since in the acid pH range the rate of hydrolysis of aminoalkyl methacrylates is very low, data for the hydrolysis in neutral and alkaline pH ranges are mainly considered below.

The first most detailed information about the kinetics of the alkaline hydrolysis of esters of *N*-alkylaminoalcohols was reported by Agren et al.[87], Hansen[88], Zaslawsky and Fischer[89], and Higuchi et al.[90]. Isolated and conflicting data concerning the mechanism of this reaction are quoted in other communications[91-95] and the influence of the structure of the esters on their reactivity has been examined[96,97]. Later studies[98-103], on the one hand, confirmed and greatly expanded the available information concerning the kinetics of the alkaline hydrolysis of the aminoalkyl esters and, on the other hand, made it possible to treat this reaction from the standpoint of the nature of the interaction of the functional groups (the amino- and ester groups); despite the hypotheses put forward[93,104,105], this problem remained open for a long time.

Many studies of the kinetics and mechanism of the hydrolysis of the aminoalkyl esters were made by pH-stat[88,89,92,106] and spectrophotometric[87,90,98,101,102,107] methods; in a few instances chromatography[108] and colorimetry[107] were used. However, in the case of esters capable of being reduced at a dropping mercury electrode, the polarographic method proved to be the most convenient and promising[99] (see Section I). The reaction is then followed on the basis of the time variation of the limiting current, proportional to the concentration of the aminoalkyl ester. The only complication which may arise when the polarographic method is used to investigate the kinetics of the hydrolysis of esters on the basis of the wave for the initial ester is the possible influence of the hydrolysis product on this wave: adsorption or other effects. An appropriate test is therefore necessary in each instance. The hydrolysis products derived from the aminoalkyl esters of $\alpha\beta$-unsaturated acids considered in the present review did not influence the polarographic wave of the initial ester[99,100]. It is noteworthy that the polarographic method has been used successfully also in the study of the kinetics of the hydrolysis of many other esters[109-114].

Since, depending on the pH of the solution, the aminoalkyl esters can exist both as neutral molecules (RN) and as species protonated at the nitrogen atom (RNH⁺), in the general case the hydrolysis of such esters can be described by the sum of the following reactions[87,88,99]:

$$\mathrm{RN}\left|\begin{array}{l}\xrightarrow[k'_{\mathrm{OH^-}}]{\mathrm{OH^-(I)}}\\[2ex] \xrightarrow[k'_{\mathrm{H_2O}}]{\mathrm{H_2O(II)}}\end{array}\right. ;\qquad \mathrm{RNH^+}\left|\begin{array}{l}\xrightarrow[k''_{\mathrm{OH^-}}]{\mathrm{OH^-(III)}}\\[2ex] \xrightarrow[k''_{\mathrm{H_2O}}]{\mathrm{H_2O(IV)}}\end{array}\right. , \tag{10}$$

where k' and k'' are the rate constants for the reactions of the non-protonated and protonated forms of the esters respectively.

Bearing in mind that the rate of hydrolysis of the aminoalkyl esters is very low in the acid pH range[71,88], the influence of reaction (IV) [mechanism (10)] may be neglected at pH ⩾ 7.[99] Therefore the hydrolytic process to which mechanism (10) refers can be described by the following kinetic equation[87-89]:

$$-\frac{\mathrm{d}C_{\mathrm{est}}}{\mathrm{d}t}=\left(k'_{\mathrm{OH^-}}C_{\mathrm{OH^-}}\frac{K_a^0}{K_a^0+a_{\mathrm{H^+}}/f_{\mathrm{RNH^+}}}+k'_{\mathrm{H_2O}}\frac{K_a^0}{K_a^0+a_{\mathrm{H^+}}/f_{\mathrm{RNH^+}}}+\right.$$
$$\left.+k''_{\mathrm{OH^-}}C_{\mathrm{OH^-}}\frac{a_{\mathrm{H^+}}/f_{\mathrm{RNH^+}}}{K_a^0+a_{\mathrm{H^+}}/f_{\mathrm{RNH^+}}}\right)C_{\mathrm{est}}=k_{\mathrm{exp}}C_{\mathrm{est}}\ , \tag{11}$$

where $k'_{\mathrm{OH^-}}$, $k'_{\mathrm{H_2O}}$, and $k''_{\mathrm{OH^-}}$ are the corresponding rate constants, K_{a}^0 is the thermodynamic acid dissociation constant of RNH⁺ (since Tur'yan and coworkers[72,73] obtained K_{a} at a comparatively low ionic strength, in the calculations below it was assumed that $K_{\mathrm{a}}^0 \simeq K_{\mathrm{a}}$), $f_{\mathrm{RNH^+}}$ the activity coefficient of RNH⁺, k_{exp} = const. at a constant pH, and C_{est} is the analytical concentration of the ester. In relation to the polarographic method, when the limiting current $\bar{i}_{\mathrm{lim}}$ of the aminoalkyl ester is directly proportional to the sum of the concentrations of its protonated and non-protonated form, i.e. to C_{est}, Eqn. (11) becomes at a constant pH

$$\frac{\mathrm{d}\bar{i}_{\mathrm{lim}}}{\mathrm{d}t}=k_{\mathrm{exp}}\bar{i}_{\mathrm{lim}}\ . \tag{12}$$

The suitability of a pseudofirst-order equation [Eqns. (11) and (12)] for the description of the kinetics of the hydrolysis of the aminoalkyl esters has been confirmed in a number of studies[88,89,99,102]. On the other hand, the fact that the hydrolysis of the aminoalkyl esters constitutes the sum of the reactions of the protonated and non-protonated forms of the ester has not been always taken into account[97]. The experimental psuedo first-order rate constants k_{exp} can be found graphically on the basis of Eqn. (11) or (12).

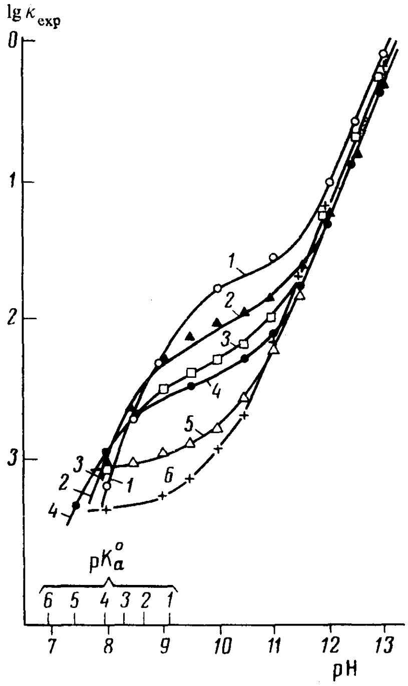

Figure 5. Variation of the experimental hydrolysis rate constant with pH.[99] Curves—experimental data; symbols—data calculated by Eqn. (13) (Table 3): 1) M–OCH₂.CH₂NHC(CH₃)₃; 2) M–OCH₂CH₂N(C₂H₅)₂; 3) M–OCH₂.CH₂N(CH₃)C₄H₉; 4) M–OCH₂CH₂N(CH₃)₂; 5) M–OCH₂.CH₂N(CH₃)CH₂–CH=CH₂; 6) M–OCH₂CH₂N(CH₂–CH=CH₂)₂.

The contribution of reactions (I)–(III) [mechanism (10)] depends on the pH of the medium in which the ester is hydrolysed and this determines the characteristic form of the lg k_{exp}–pH curves obtained[90,98,99] in studies of the rate of hydrolysis of the aminoalkyl esters over a wide pH range. These curves (Fig. 5) have two steep sections with an intervening low-slope section. Fig. 5 shows that, in the region where pH ≫ pK_{a}^0, reaction (I) predominates (the upper steep section represents the linear dependence of lg k_{exp} on pH with a slope close to unity): at pH values close to pK_{a}, the rate constant k_{exp} varies insignificantly with pH, which suggests a dominant contribution of either stage (II) or stage (III), since in both cases there should be a low-slope section of the $\lg k_{exp}$–pH relation, i.e. these stages are kinetically indistinguishable[88,99] [Eqn. (11)]. In agreement with experimental data and the theory[99] [Eqn. (11)], the low-slope section of the $\lg k_{exp}$–pH curves is displaced more towards lower values of k_{exp} and pH the lower the value of pK_a^0. At pH ≪ pK_a^0 the lower steep linear section is observed in the plot of $\lg k_{exp}$ against pH with a slope close to unity, which shows that stage (III) predominates in this instance [Eqn. (11)], provided that RN has been almost completely converted into RNH^+. For aminoalkyl esters with a low value of pK_a^0, it proved impossible to observe experimentally the lower steep section (Fig. 5).

Table 3. The rate constants for the alkaline hydrolysis of the aminoesters $CH_2{=}C(CH_3)COOCH_2CH_2R$ (H_2O; 25°C; ionic strength 0.5; polarographic method[99,100]).

R	pK_a	k'_{OH^-}, litre mole^{-1} min^{-1}	k''_{OH^-}, litre mole^{-1} min^{-1}
$NHC(CH_3)_3$	9.12	4.5±0.5	435±40
$N(C_2H_5)_2$	8.66	3.1±0.6*	550±90**
$N(CH_3)C_4H_9$	8.28	3.4±0.3	670±50
$N(CH_3)_2$	7.94	2.5±0.1	990±40
$N(CH_3)CH_2CH{=}CH_2$	7.39	3.4±0.2	1280±90
$N(CH_2CH{=}CH_2)_2$	6.93	3.9±0.2	1450±100
H		2.1±0.0	—
$\overset{+}{N}(CH_3)_3$		35.9±0.3	—

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* $E'_{act}(k'_{OH^-}) = 12.1 \pm 0.4$; $\lg A' = 7.6 \pm 0.5$ (E_{act} is the activation energy in kcal mole^{-1} and A is the pre-exponential factor).

** $E''_{act}(k''_{OH^-}) = 19.9 \pm 2.3$; $\lg A'' = 16.0 \pm 1.6$.

In the solution of the problem of the separate determination of the rate constants for the kinetically indistinguishable stages (II) and (III), it has been shown[88] on the basis of a comparison with the kinetics of the hydrolysis of 2-dialkylaminoethyl bromides that the influence of stage (II) may be neglected. Comparison of the rates of hydrolysis of acetylcholine, ethyl acetate, and diethylaminoethyl acetate in neutral and alkaline solutions also led to the qualitative conclusion[39] that stage (III) predominates. A similar conclusion has been arrived at by a more rigorous procedure (by analysing the influence of the ionic strength of the solution on the kinetics of the hydrolysis).[99] Thus in the general case the hydrolysis of the aminoalkyl esters is described by reactions (I) and (III) [mechanism (10)] and Eqn. (11) can be written as follows:

$$k_{exp} = k'_{OH^-}C_{OH^-}\frac{K_a^0}{K_a^0 + a_{H^+}/f_{RNH^+}} + k''_{OH^-}C_{OH^-}\frac{a_{H^+}/f_{RNH^+}}{K_a^0 + a_{H^+}/f_{RNH^+}}. \qquad (13)$$

The applicability of Eqn. (13) has also been confirmed[99] by comparing the experimental and calculated kinetic curves (Fig. 5).

The second-order rate constants, calculated by Eqn. (13) for aminoalkyl methacrylates[99,100], and most reliable data[87–89,92,101,102,115] for other aminoalkyl esters are listed in Tables 3–5.

One should note that, in the study of the kinetics of the hydrolysis of the aminoalkyl esters in buffer systems, general alkaline catalysis is sometimes possible. The effect of acetate and phosphate ions on the kinetics of the hydrolysis of choline esters and esters with a tertiary alkylamino-group has been investigated. However, in the case of choline esters[98,107,116,117] as well as esters with a tertiary amino-group[94,107] this effect could be observed only under conditions where the influence of more effective catalysts is slight (pH 5–6) and for esters with a tertiary amino-group the contribution of the catalytic effect of the components of the buffer mixture to the overall hydrolysis rate constant was insignificant[71,90,94,118,119].

Table 4. The rate constants and activation parameters for the alkaline hydrolysis of the aminoesters $C_6H_5.$ $.COOCH(R)(CH_2)_nNR'_2$ (60°C; 30 wt.% aqueous ethanol; ionic strength 0.1; spectrophotometric method[101,102]).

n	R	R′	pK_a	k'_{OH^-}, litre mole^{-1} min^{-1}	E'_{act}, kcal mole^{-1}	$\lg A'$	k''_{OH^-}, litre mole^{-1} min^{-1}	E''_{act}, kcal mole^{-1}	$\lg A''$
1	H	CH_3	7.24	6.75±0.09	12.6±1.1	7.3	9 000±1200	11±1	9.4
1	H	C_2H_5	7.73	7.9±0.2	12.5±2.0	7.3	5 900±480	14±1	11.1
2	H	CH_3	7.67	7.6±0.5	10.7±0.3	6.1	2 100±120	11±1	8.7
2	H	C_2H_5	8.41	6.7±0.5	11.6±0.3	6.6	780±120	14±1	10.2
1	C_6H_5	CH_3	6.30	1.84±0.06	11.5±0.2	6.0	76 000±8400	17±3	14.2
1	C_6H_5	C_2H_5	7.00	1.52±0.03	9±1	4.3	26 400±1800	10±2	9.5
2	C_6H_5	CH_3	7.32	1.15±0.02	9.4±0.2	4.4	2 580±120	16±2	12.1
2	C_6H_5	C_2H_5	8.07	0.86±0.06	6.2±2.0	2.2	469±42	7±1	5.4
3	C_6H_5	CH_3	8.00	0.82±0.02	7.0±1.5	2.7	2 210±240	13±1	10.0
—	$C_6H_5COOCH_2CH_3$			3.68±0.06					

Table 5. The rate constants for the alkaline hydrolysis of the aminoesters $RCOO(CH_2)_nN(R')_2$ (25°C; H_2O; pH-stat method).

n	R	R′	k'_{OH^-} litre mole^{-1} min^{-1}	k''_{OH^-}, litre mole^{-1} min^{-1}	Ionic strength	References
2	CH_3	CH_3	6.0	2 560	0.07	88
3	CH_3	CH_3	8.4	350	0.07	88
2	C_6H_5	C_2H_5	2.5	1 580*	—	87
2	CH_3	C_2H_5	—	31 000**	0.006	89
2	C_2H_5	CH_3	—	14 400	0.1	92
—	$C_6H_5COOC{\equiv}CCH_2(C_2H_5)_2$		7.46***	167	—	115

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* Spectrophotometric method.

** 60°C.

*** Aqueous ethanol.

2. Hydrolysis of Aminoalkyl Esters in the Non-Protonated Form. The Influence of the Structure of the Ester

The introduction of an amino-group into the ethyl methacrylate molecule leads to an acceleration of the hydrolysis of the ester (Table 3). Such acceleration relative to analogues without an NR_2 group in the alcohol residue has also been observed for esters of azobenzene carboxylic[120], glycolic[96], acetic[88,89,96], and benzoic[87,93,101] acids. However, the influence of the amino-group on the reactivity of the esters is small and cannot be explained by the postulated[93,98,105] activation of the carbonyl bond by the intramolecular interaction of the

β-nitrogen atom with the carbonyl carbon atom, i.e. N: → C=O. It was concluded[88,89,99-101,103,121] that there is no nitrogen–carbonyl interaction and that the inductive effect of the non-protonated alkylamino-group predominates. This conclusion was based on the following characteristics of the influence of the structure: (1) as regards the general relation between lg k_{OH^-} and σ^*_{R} obtained for methacrylates with various alkoxy-groups, the aminoalkyl ester behaves in the nonprotonated form as an ordinary alkyl ester in accordance with the value of its σ^*_{R};[100] (2) a change in the basicity of the amino-group does not affect significantly the rate of hydrolysis of the non-protonated forms of the aminoalkyl esters, as shown by the absence[99,101] of an appreciable influence of the nature of the substituents at the nitrogen atom in the alkoxy-group (Tables 3 and 4); (3) the influence of the basicity of the carbonyl group on the reactivity of the non-protonated forms of aminoalkyl esters with a variable acid component and of the ethyl esters of substituted benzoic acids is approximately the same[103]; (4) studies on infrared spectra showed[121] that the frequencies and intensities of the band associated with the vibrations of the C=O bond in aminoesters and their analogues without an amino-group in the alkoxy-moiety do not differ appreciably from one another, while in the case of the postulated nitrogen–carbonyl interaction the differences should have been significant.

It is interesting to note that an appreciable variation of the activation energy with the number of methylene units and with the nature of the substituent at the nitrogen atom has been noted for esters of secondary benzyl alcohols containing a tertiary amino-group in the alkyl chain, in contrast to esters of primary aminoalkyl carbinols[101]. These data can be accounted for[101] by the nucleophilic catalysis by the amino-group, i.e. by the direct interaction of the amino- and ester groups. However, since spectroscopic evidence was not obtained for such interaction, the authors[101] suggested that the interaction is manifested mainly in the transition state and not in the initial state.

Other structural characteristics of esters in the non-protonated form which have been observed[101] include a distinct decrease of reactivity on passing from esters of primary aminoalcohols to those of secondary aminoalcohols and further to esters of tertiary aminoalcohols as well as a decrease of reaction rate with increase in the length of the hydrocarbon chain by a CH_2 group in the alcoholic component of the ester[88,96,101], which has been explained by steric hindrance[96].

3. Hydrolysis of Aminoalkyl Esters Protonated at the Nitrogen Atom. The Influence of the Structure of the Ester

It has been shown for esters of various acids[87-89,99,102,115] that the protonation of the amino-group increases the reactivity of the esters by 2–3 orders of magnitude compared with the initial non-protonated esters and their analogues without an NR_2 group in the alkoxy-moiety (Tables 3–5).

Such acceleration of the hydrolysis of the protonated ester can in general be a result of three effects: (a) the powerful inductive effect of the $+NHR'R''$ group via the chain of carbon atoms ($\sigma^* \simeq 3$);[122] (b) the electrostatic effect of the positive charge on the nitrogen atom (the interaction of N^+ with the C=O group); (c) the effect of the intramolecular hydrogen bond (IAHB) $^+NH\ldots O=C$.

These effects can be separated and their contributions to the overall acceleration of the hydrolysis can be estimated quantitatively with the aid of correlation analysis[123] using the principles described by Palm et al.[124] and assuming that each effect is independent of the structure of the acyl residue. In this case the inductive effect, calculated from the data of Ignat'eva et al.[100], accelerates the reaction by a factor of 4–5 and the electrostatic effect, determined for the $^+N(CH_3)_3$ group, accelerates it by a factor of 5–6. Bearing in mind that the values of σ^* and the electrostatic effects for the $^+NR_3$ and $^+NHR'R''$ groups are approximately the same, the difference by a factor of 15–40 between the values of k_{OH^-} for compounds with the $^+NR_3$ and $^+NHR'R''$ groups can be regarded as a result of the catalytic effect of the intramolecular hydrogen bond. The inductive effect and other factors have been shown by a computational procedure to exert their influence in the same order[88,100,102].

The hypothesis of the intramolecular interaction of the carbonyl and protonated amino-groups via hydrogen bonding, put forward for the first time by Shätzle et al.[93], has been used by many investigators[87,88,124-126] to explain the acceleration of the hydrolysis of the protonated forms of the aminoesters. However, convincing evidence for such interaction was obtained only in studies of the structural influences on the reactivities of the aminoesters[88,89,99,100,102,115,127].

The following characteristics of the influence of the structure confirm this hypothesis. (1) An increase of k''_{OH^-} with decrease of pK_a for the aminoester has been observed[88,99,102]. Since the energy of the hydrogen bond depends on the acidity of the dialkylammonium groups, it was natural to suppose that the decrease of pK_a should lead indirectly to an increase of the strength of the intramolecular hydrogen bond and hence to an enhancement of the catalytic effect of the $^+NHR'R''$ group, causing the increase of k''_{OH^-}. This has been confirmed by the linear variation of lg k''_{OH^-} with pK^0_a, observed by Tur'yan et al.[99]. It has been suggested[102] that, following the introduction of a phenyl residue into aminoethyl ester molecules (in contrast to aminopropyl esters, the $-I$ effect in the α-position of the alkoxy-group accelerates the reaction for the same reason, while the inductive effect of the C_6H_5 group on the carbonyl atom should be the same regardless of the length of the chain between the carboxy- and amino-groups. (2) The increase in the length of the chain between the nitrogen atom and the ester group by one CH_2 unit decreases k''_{OH^-} by a factor of 4–8, while the expected decrease due to the inductive effect is by a factor of 7–15.[102]. (3) The effect of the spatial proximity of the ammonium and ester groups, discovered by Babaeva et al.[127] on comparing the rates of hydrolysis of esters of the ethylene and acetylene series,

$$\Delta \lg k''_{\mathrm{OH}^-} = \lg k''_{\mathrm{OH}^-(\overset{+}{\mathrm{N}}\mathrm{HR'R''})} - \lg k_{\mathrm{OH}^-(\overset{+}{\mathrm{N}}(\mathrm{CH}_3)_3)},$$

is responsible for the increased reactivity of the protonated forms of the aminoester. When such proximity was hindered, the difference between the rate constants for the $^+NR_3$ and $^+NHR'R''$ derivatives was not greater than by a factor of 1.5–2. (4) The observed correlation[100] between $\Delta \lg k''_{\mathrm{OH}^-}$ ($\Delta \lg k''_{\mathrm{OH}^-(\overset{+}{\mathrm{N}}\mathrm{HR'R''})} = \lg k''_{\mathrm{OH}^-(\overset{+}{\mathrm{N}}\mathrm{HR'R''})} - \lg k_{\mathrm{OH}^-[\overset{+}{\mathrm{N}}(\mathrm{CH}_3)_3]}$) and the sum of the Taft constants $\Sigma\sigma^*_{\mathrm{R_i}}$ of the substituents at the nitrogen atom also constitutes significant confirmation of the influence of the

$^+$NHR′R″ group via intramolecular hydrogen bonding. The similarity of the values of ρ^* in the relations between $\lg k'_{\mathrm{OH}^-}$ and σ^*_{R} (for esters with a variable alkoxy-group) and between $\Delta \lg k''_{\mathrm{OH}^-}$ and $\Sigma\sigma^*_{\mathrm{R}}$ led to the conclusion[100] that the efficiences of the transmission of influences via the chain of carbon atoms and via the intramolecular hydrogen bond are approximately the same.

Thus the intramolecular interaction between the carbonyl and ammonium groups, transmitted via the hydrogen bond, is dominant in the acceleration of the hydrolysis of the protonated aminoester. However, the mechanism of this interaction between the functional groups cannot be accounted for by a change in the electron density at the carbonyl carbon atom, as suggested by some investigators[88,128]. The study of the activation parameters (activation energy and the pre-exponential factor)[71,102] showed that the acceleration of the reaction of the protonated aminoester owing to intramolecular hydrogen bonding is most probably associated with the interaction of the solvent with the initial and transition states in the reaction and that the main influence of the hydrogen bond is most probably manifested in the transition state, where it facilitates proton transfer from $\mathrm{N^+H}$ to $\mathrm{O^-}$ [see the process mechanism below; stage (II) in mechanism (17)], rather than in the initial state. The latter factor leads to a decrease of the degree of solvation of the transition state and hence to a change in solvation entropy. Data obtained in a study[103] of the infrared spectra in the region corresponding to the vibrational band of the C=O bond of aminoesters, characterising the initial state of the ester group, as well as the results of a ^{1}H NMR study[129] of the $\overset{+}{\mathrm{N}}\mathrm{H}\ldots\mathrm{O{=}C}$ interaction agree with the conclusion that there is no hydrogen bond in the initial state of the protonated aminoester[102]. Although the ^{1}H NMR data were obtained in chloroform and cannot be transferred mechanically to aqueous solutions in which the hydrolysis was studied, they also support the view that there is no intramolecular hydrogen bond in the initial state of the aminoester molecule (the earlier attempts at a direct determination of the strength of the hydrogen bond[130] were unsuccessful).

4. Kinetics of the Hydrolysis of the Aminoalkyl Esters in a Two-phase Water–Organic Liquid Emulsion

The study of the kinetics of chemical reactions in multiphase systems is of great theoretical and practical interest[131-133]. The theoretical and experimental principles of the application of the polarographic method in the study of the kinetics of chemical reactions in a two-phase emulsion system (water–benzene), including the study of the kinetics of the hydrolysis of aminoesters in such a system[135], were examined for the first time by Tur'yan et al.[134]. This type of system makes it possible to simulate to some extent the conditions of emulsion polymerisation[134] and this is very important from the practical point of view. On the other hand, owing to the rapid establishment of the equilibrium distribution of the components in the emulsion (large contact area), it is possible to test important theoretical relations for the kinetics of reactions in multiphase systems[134].

A polarographic study of the kinetics of the hydrolysis of aminoesters in a two-phase water–organic liquid emulsion has been made[135] and data have been obtained[135] for the equilibrium distribution of the aminoester between the aqueous and benzene phases, these being necessary for a theoretical interpretation of the kinetic measurements and for the development of a polarographic method whereby the aminoester can be determined (see below).

It has been shown[135] that in the general case the distribution of the aminoester between the aqueous and benzene phases is complicated by the dissociation of the protonated aminoester in the aqueous phase and, regardless of the pH of this phase, virtually only the non-protonated form of the aminoester is distributed in the water–benzene emulsion. These conclusions have been justified experimentally by the following findings: (1) the dependence of the partition coefficient $(K_\mathrm{c})_\mathrm{A}$ on the pH of the aqueous phase; (2) the suitability for the calculation of the partition coefficient of the expression

$$(K_c)_\mathrm{A} = \frac{(C_\mathrm{RN})_\mathrm{B}(K_a + a_{\mathrm{H^+}}/f_{\mathrm{H^+}})}{K_a\,(C^0_\mathrm{est})_{\mathrm{H_2O}}}, \tag{14}$$

where $(K_\mathrm{c})_\mathrm{A}$ is the ratio of the equilibrium concentrations of the non-protonated form of the aminoester in the aqueous and benzene phases. Eqn. (14) has been obtained taking into account the equilibrium between the protonated and non-protonated aminoester forms; the concentration of the latter is expressed in terms of the acid dissociation constant of the aminoester and its experimental overall concentration in the aqueous phase $(C^0_\mathrm{est})_{\mathrm{H_2O}}$. The partition coefficient calculated in this way (Table 6) was constant.

Table 6. The partition coefficient and the rate constants for the hydrolysis of diethylaminoethyl methacrylate in the water–benzene system at 25 °C (polarographic method)[135].

$(K_\mathrm{c})_\mathrm{A}$	k_1^{EM}, min^{-1} (expt.)	k_1^{EM}, min^{-1} (calc.)	$k_1^{\mathrm{H_2O}}$, min^{-1}
210±1.6	$9.9\cdot10^{-5}$	$9.3\cdot10^{-5}$	$1.1\cdot10^{-2}$

Alkaline hydrolysis of aminoesters in the emulsion at a constant pH is a pseudomonomolecular process and is described by the equation for first-order kinetics with respect to the aminoester[135].

A kinetic equation suitable for the polarographic study of the kinetics of chemical reactions in a two-phase system under the conditions of the equilibrium distribution of the components has been obtained[134] on the basis of the study of Abramzon and Kogan[133]. The equilibrium conditions are quite reliably realised in the case of an emulsion[134,135]. The above equation for the pseudomonomolecular alkaline hydrolysis of the aminoester in the emulsion (bearing in mind that the reaction proceeds virtually only in the aqueous phase and the concentration of $\mathrm{OH^-}$ ions in the benzene phase is insignificant) is of the following form[135]:

$$\lg \bar{i}_\mathrm{lim} = \mathrm{const} - \frac{1}{2.3}\,\frac{V_1 k_1^{\mathrm{H_2O}}}{V_1 + V_2 (K_c)_\mathrm{A}}\,t = \mathrm{const} - k_1^{\mathrm{em}} t, \tag{15}$$

where t is the duration of hydrolysis, V_1 and V_2 are the volumes of the aqueous and benzene phases respectively, and $k_1^{\mathrm{H_2O}}$ is the rate constant for alkaline hydrolysis in the aqueous buffer solution at the same pH and ionic strength as in the aqueous phase of the emulsion.

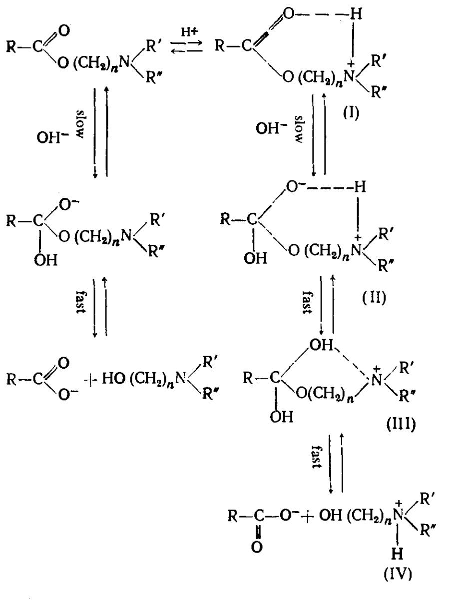
The sharp decrease of the effective rate constant in the emulsion (k_1^{em}),

$$k_1^{em} = \frac{1}{2.3} \cdot \frac{V_1 k_1^{H_2O}}{V_1 + V_2 (K_c)_A} \quad , \qquad (16)$$

compared with the aqueous medium (Table 6) has been explained by the redistribution of the reactants between the phases: the aminoester passes almost completely to the benzene phase [$(K_c)_A = 210$], while the hydrolysis proceeds in the aqueous phase. The validity of the theoretical postulates has been confirmed by the similarity of the experimental effective rate constant for the hydrolysis of the aminoester in the water–benzene emulsion and the value calculated by Eqn. (16).

5. The Mechanism of the Hydrolysis

The alkaline hydrolysis of the aminoalkyl esters (in both protonated and non-protonated forms) by hydroxide ions proceeds via a bimolecular $B_{AC}2$ mechanism (according to Ingold's classification)[136] and, when account is taken of the nature of the interaction of the functional groups discussed above, the overall reaction can be described by the following scheme[71,99,102]:



(17)

IV. THE KINETICS AND MECHANISM OF ISOMERISATION

1. Process Kinetics

In a series of acryl derivatives of aminoalkanols, aminophenols, and other compounds containing in the molecule both the hydroxy-group and primary or certain secondary amino-groups, the O–N migration of the acyl group is a well known phenomenon[95,105,137-144], but most studies on the latter have been qualitative or semiquantitative.

The results obtained at the beginning of the 1960s led to the conclusion that esters containing a primary or secondary amino-group can as a rule exist only in the protonated form, the free bases rearranging to the corresponding amides[95,105,139-144]. It has been established that the process is intramolecular, the dependence of the rate of reaction on the pH of the medium has been demonstrated, and the hypothesis has been put forward that an intermediate compound of the type of hydroxyoxazolidine is formed in the reaction.

A number of studies have been made on the reaction kinetics[52,126,145-147]. The kinetics of the O–N isomerisation of *O*-acetylethanolamine to *N*-acetylethanolamine have been studied by the pH-stat method in the pH range from 7.0 to 9.7.[126] Using a spectrophotometric method, the same reaction was studied in a buffer system at pH 7.9, 8.2, and 8.5.[146]

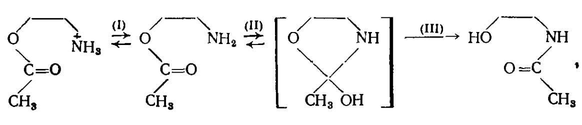
The O–N migration of the acyl group in a series of aminoalkyl methacrylates in the pH range 8.0–10.5 has been investigated in detail by the polarographic method[52,147]. This method proved to be the most promising when the aminoesters are capable of being reduced at a dropping mercury electrode (as in the study of their hydrolysis; see Sections I and III). The process in the buffer solution, where the aminoesters investigated give rise to polarographic reduction waves, was followed directly from the time variation of the limiting current, which is directly proportional to the concentration of the aminoester (the sum of the concentrations of the protonated and non-protonated forms).

The use of the polarographic method also made it possible to elucidate the influence of the simultaneous hydrolytic reaction, which was done using a different supporting electrolyte: a buffer solution at pH 4.75 containing 5% of formaldehyde[148-152]; the reduction wave of both the initial aminoester and of the hydrolysis product (the corresponding aminoalcohol) was observed in this solution[52,147]. Comparison of the results of the polarographic study in the presence and absence of formaldehyde in the solution led to the conclusion[52,147] that the hydrolysis has an extremely insignificant influence on the isomerisation kinetics. The same conclusion concerning 2-aminoethyl acetate was reached in another study[126] based on pH-stat data.

It has been noted[52,126,146,147] that the acyl group does not migrate in the protonated form of the aminoester, since nucleophilic attack by the protonated amino-group on the carbonyl carbon atom bearing a partial positive charge is unlikely. The reaction is both catalysed by hydroxide ions[52,126,146,147] and is subject to general base catalysis[146,147].

The isomerisation kinetics at constant pH are described by a first-order equation with respect to the aminoester[52,126,146,147]. Using the polarographic method, the experimental rate constants k_{exp} can be found by means of Eqn. (12) from a plot of $\lg \bar{i}_{lim}$ against t. Division by the coefficient $p = K_a/\{K_a + [H^+]\}$ (K_a is the acid dissociation constant of the aminoester), defined as the fraction of the non-protonated form of the aminoester, yields the rate constant referred to the non-protonated form.

The variation of $\lg(k_{exp}/p)$ with pH is illustrated in Fig. 6. On the basis of Hansen's experimental results[126], it has been shown[153] that the above relation has a similar form for the isomerisation of 2-aminoethyl acetate. The complexity of the dependence of the rate of rearrangement on the pH could not be accounted for by Hansen's mechanism[126]:



(18)

according to which stage (III) is catalysed by hydroxide ions and the rate-limiting stage varies with pH: stages (III) and (II) are rate-limiting at low and high pH values respectively.

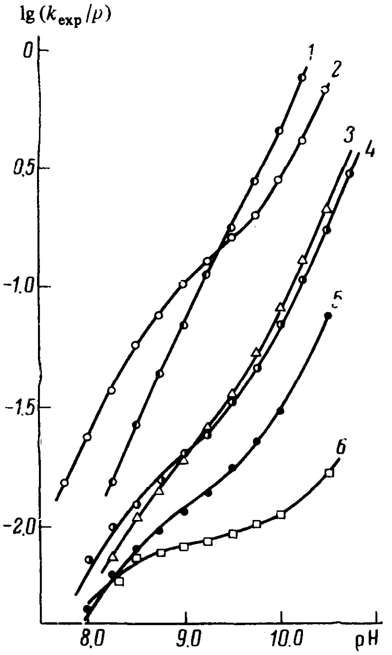
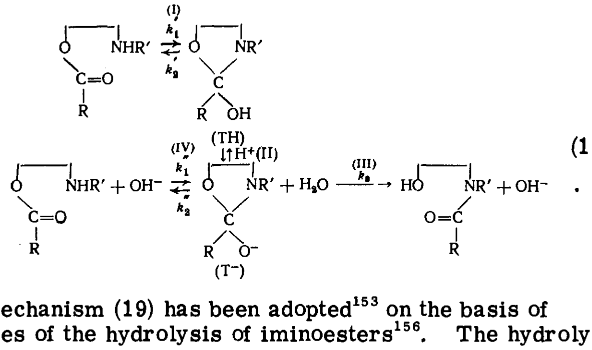


Figure 6. Variation with pH of the experimental isomerisation rate constant referred to the non-protonated form of the aminoester[52,147]. Symbols—experimental data; curves—calculated data: 1) $M-OCH_2CH_2NHCH_3$; 2) $M-OCH_2CH_2NH_2$; 3) $M-OCH_2CH_2NHC_2H_5$; 4) $M-OCH_2CH_2NHC_4H_9$-n; 5) $M-OCH_2CH_2NHC_4H_9$-iso; 6) $M-OCH_2CH_2NHC_3H_7$-iso.

The most probable mechanism, which can account for the O-N migration of the acyl group[52,147,153] is analogous to the mechanism of the aminolysis of esters[153-155] and can be described by the following scheme[52,147]:



(19)

Mechanism (19) has been adopted[153] on the basis of studies of the hydrolysis of iminoesters[156]. The hydrolysis of iminoesters and the aminolysis of esters are accompanied by the formation and cleavage of the same types of intermediates.

In contrast to the studies by Hansen[126] and Martin et al.[146], in mechanism (19) account is taken of two forms of the intermediate—the undissociated form (TH) and the anion (T^-). It has been shown[153] that the undissociated form is not converted directly into the amide. Application of the method of steady states with respect to $[TH] + [T^-]$ in relation to the polarographic method yielded the following kinetic equation[52,147]:

$$\frac{d\bar{i}_{\lim}}{dt} = \frac{(k_1' + k_1''[OH^-])\,k_3\frac{K_1}{[H^+]}}{k_2' + (k_2'' + k_3)\frac{K_1}{[H^+]}}\,\frac{K_a}{K_a + [H^+]}\,\bar{i}_{\lim}, \tag{20}$$

where K_1 is the acid dissociation constant of TH; the rate constants k_2'' and k_3 include the concentration of water. k_1' includes not only the rate constant for the non-catalysed stage but also the kinetic terms associated with catalysis by the HPO_4^{2-} and CH_3COO^- ions of the universal buffer mixture[147]. At pH 8–10.5 these terms are almost independent of the pH, since the concentrations of the above ions change insignificantly in this range; therefore the rate constant k_1' can be referred to by convention as the rate constant of the non-catalysed stage. It has been shown[52,147] that the catalytic effect of the borate anion may be neglected.

Eqns. (12) and (20) with $[H^+]$ replaced by $[OH^-]$ yielded the relation describing the experimental rate constant for the migration of the acyl group in the non-protonated form of aminoalkyl methacrylates[147]:

$$\frac{k_{exp}}{p} = \frac{(k_1' + k_1''[OH^-])\,(k_3K_1/k_2'K_w)\,[OH^-]}{1 + \frac{(k_2'' + k_3)\,K_1}{k_2'K_w}[OH]^-}, \tag{21}$$

where K_W is the ionic product of water. In conformity with both experiment[52,147] and theory, k_{exp} = const. at constant pH. Eqn. (21) can be rearranged to the linear relation

$$\frac{k_{exp}}{p\,[OH^-]} = a + b\,[OH^-] - c\,\frac{k_{exp}}{p}, \tag{22}$$

where

$$a = k_1'\frac{k_3K_1}{k_2'K_w}; \tag{23}$$

$$b = k_1''\frac{k_3K_1}{k_2'K_w}; \tag{24}$$

$$c = \frac{(k_2'' + k_3)\,K_1}{k_2'K_w}. \tag{25}$$

Hence, taking into account mechanism (19), we have

$$k_1' = \frac{a^2}{ac - b}; \tag{26}$$

$$k_2'' = \frac{ab}{ac - b}. \tag{27}$$

The kinetic parameters of the O–N rearrangement of the acyl group in aminoalkyl methacrylates, including the rate constants k_1' and k_1'' (Table 7), have been calculated[147] on a computer from experimental data by Eqns. (22)–(27) (Fig. 6). Solution[153] of an equation of type (20) yielded k_1' = 0.13 min^{-1} and k_1'' = 1.08 × 10^4 litre $mole^{-1}$ min^{-1} for aminoethyl acetate.

Mikhlin et al.[147] (Fig. 6) and Schmir[153] showed that the calculated lg (k_{exp}/p)–pH curves agree satisfactorily with the experimental curves. Like the kinetic curves for the hydrolysis of aminoesters, these plots are characterised by three sections: the lower and upper sections (which are steeper and approach a straight line with a slope of unity) and the middle section (with a lower slope). This type of kinetic relation has been explained [mechanism (19)] [52,147] taking into account the different effects on the process, as a function of the pH, of the non-catalysed stage (I) and the simultaneous stage (IV) catalysed by OH^- ions and also taking into account the changes in the rate-limiting stage as a function of the pH.

Table 7. The kinetic parameters of the O–N migration of the acyl group in aminoalkyl methacrylates[147] $\mathrm{M{=}CH_2{=}C(CH_3)C}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow O\\ \searrow\end{smallmatrix}$.

Ester	$10^{-3}a$	$10^{-7}b$	$10^{-5}c$	$10^2k_1'$, min^{-1}	k_1'', litre $mole^{-1}$ min^{-1}	pK_a*
$M—OCH_2CH_2NH_2$	22.5±0.5	23.6±2.10	1.74±0.09	13.8	1450	8.70
$M—OCH_2CH_2CH_2NH_2$	2.34±0.02	1,98±0.075	0.32±0.01	9.8	830	9.62
$M—OCH_2CH_2NHCH_3$	6.86±0.11	10.8±0.8	0.38±0.02	31.0	4900	8.96
$M—OCH_2CH_2NHC_2H_5$	4.51±0.19	10.1±0.9	2.27±0.17	2.2	530	9.15
$M—OCH_2CH_2NHC_4H_9$-n	7.37±0.41	1.48±0.14	3.82±0.32	2.0	410	9.09
$M—OCH_2CH_2NHCH_2{=}CH_2$	2.56±0.11	2.41±0.17	1.31±0.11	2.1	200	8.36
$M—OCH_2CH_2NHC_4H_9$–iso	4.96±0.21	6.07±0.46	4.10±0.25	1.25	150	8.91
$M—OCH_2CH_2NHC_3H_7$–iso	8.33±0.21	1.83±0.07	9.38±0.27	0.91	20	9.13

* The values of K_a were taken from Dokolina et al.[73]

2. The Rate of Isomerisation and the Influence of the Structure of the Aminoester

The influence of the structure of aminoalkyl methacrylates on k_1'' has been analysed on the basis of the results of Mikhlin et al.[147] It has been established that the nature of the alkyl substituents at the nitrogen atom has the opposite influence on the isomerisation rate constant compared with their influence on the nucleophilic reactivity of the nitrogen atom in the amino-group. This cannot be explained by hypothesis that the rate-determining stage involves the abstraction of a proton from the amino-group, based on the Taft inductive effect[157], because the compound with the allyl substituent deviates appreciably from the correlation, and, furthermore, the coefficient ρ^* is found to be unrealistically large.

This behaviour of the above compounds, as in other reactions of amines with electrophilic agents[158-160], can be explained by the influence of steric effects. It was noted previously[144] that the steric factor can have a decisive influence on the rate of the O–N migration of the acyl group and that aminoalkyl methacrylates with a t-alkyl group at the nitrogen atom of a secondary amino-group or with a primary amino-group at a tertiary carbon atom do not undergo isomerisation at all[161,162]. The ability of arylaminoalkyl methacrylates and acrylates to exist without O–N isomerisation can be accounted for by the steric effect in combination with the reduced nucleophilicity of the nitrogen atom in the secondary arylamino-group[164].

The use of Eqn. (28), which takes into account not only the Taft[157] steric effects[165,166] but also the steric effect of the "sixth" atom, revealed[52,247] a satisfactory correlation (Table 8) with respect to k_1'':

$$\lg k_1'' = \lg k_0 + \rho^*\sigma^* + \delta E_s^c + \gamma\Delta\sigma. \qquad (28)$$

Best results were obtained with E_s^c and E_s^0; the correlation with E_s was much less satisfactory.

A satisfactory correlation has also been obtained[147] using the Swain–Scott equation[165]:

$$\lg k = a + sn = (-18.4 \pm 3.9) + (4.2 \pm 0.8)\,n; \quad (r = 0.935;\ S = 0.252). \qquad (29)$$

The nucleophilicities in Eqn. (29) were taken from Hall's paper[166] for the corresponding primary amines. The aminoester with a primary amino-group deviates from the correlation.

The rate constant for the isomerisation of 2-aminoethyl methacrylate is higher than for 2-aminopropyl methacrylate, which can be explained by the more powerful influence in the former instance of the inductive effect of the amino-group via the chain of carbon atoms.

In conclusion one should note that the rate of migration of the acyl group in 2-aminoethyl methacrylate[147] is lower than the rate of the analogous reaction for 2-aminoethyl acetate[126,153] owing to the conjugation effect.

Table 8. The parameters of the correlation based on Eqn. (28).[147]

Steric constant	$\lg k_0$	ρ^*	δ	γ	r	S
E_s^c	3.63±0.06	−2.10±0.22	1.75±0.09	0.144±0.011	0.998	0.041
E_s^0	3.64±0.07	−1.98±0.29	1.99±0.13	0.166±0.015	0.997	0.055
E_s	3.20±0.26	−8.13±3,54	3.26±1.17	0,33±0.11	0.939	0.258

V. ANALYTICAL APPLICATIONS

The ability of aminoalkyl esters of $\alpha\beta$-unsaturated acids to be reduced at a dropping mercury electrode has been used in the development of polarographic methods for the analysis of the esters. The polarography is usually carried out with quaternary ammonium salts as the supporting electrolytes in non-aqueous solvents (methanol, ethanol, and dimethylformamide).

A polarographic method for the determination of monomeric aminoalkyl acrylates and methacrylates in the presence of their polymers and copolymers with *N*-vinylcarbazole has been proposed[68,69]; a 0.05 M solution of $(C_2H_5)_4NI$ in dimethylformamide was used as the supporting electrolyte.

The possibility of the polarographic determination of diethylaminoethyl methacrylate in a mixture with acrylonitrile using a 0.025 M solution of $(C_2H_5)_4NI$ in methanol as the supporting electrolyte has also been demonstrated[86]. A method for the determination of the residual monomeric diethylaminoethyl methacrylate in the latex has been described[65]; it is based on the extraction of the aminoester from the reaction mixture with benzene and its subsequent polarography in a solution of a tetraalkylammonium salt in a benzene–ethanol mixture. As stated above, owing to the high partition coefficient, quantitative extraction is simple and rapid[65].

In contrast to non-aqueous solutions of tetraalkylammonium salts, a more readily available electrolyte—the universal buffer solution (pH 7.5) in which NaOH has been replaced by LiOH in order to obtain a more distinct threshold of the wave—has been proposed[65] as the supporting electrolyte. The method is based on the selection of the optimum pH, concentrations of the buffer components, and the ionic strength of the supporting buffer solutions.

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Application of the Mass Spectrometry of Negative Ions to Organic Chemistry

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Experimental work on the dissociative capture of electrons by organic molecules is surveyed, and the main processes involved in the interaction between such molecules and electrons are discussed. Special attention is paid to the specificity of mass spectra. The mass spectrometry of negative ions not only supplements traditional mass spectrometry but also enables several novel problems to be solved. A list of 100 references is included.

CONTENTS

I. INTRODUCTION

The formation of negative ions by interaction between electrons and molecules has been less investigated than has the formation of positive ions, although experimental study of the capture of electrons by molecules with mass-spectrometric recording of the negative ions was begun as early as the 1930s, at the same time as study of the formation of positive ions. This was due to the absence of reliable methods for the mass-spectrometric investigation of negative ions and the experimental difficulties of working with such ions. However, discovery of the ability of negative ions to excite vibrational and rotational levels of molecules in radiation-induced reactions, by the elastic and inelastic resonant scattering of electrons, has caused the recent increase in the number of publications on the formation of negative ions.

The study of negative ions has shown a general tendency for increasingly complicated species to be investigated. Whereas in the 1950s simple diatomic and triatomic molecules were examined almost exclusively, at the present time increasing attention is being paid to complex molecules, including those of organic compounds. It is also planned to use mass spectra of negative ions to solve structural and analytical problems of organic chemistry.

Progress in the theory of resonances accompanying interaction between electrons and molecules[1-6], as well as development of electron-impact spectrometry[7], increased the interest taken in the capture of electrons by molecules with the formation of negative ions. At the same time advances in experimental technique promoted the development of improved methods of examining negative ions. The monochromatisation of electrons[8,9], enhancement of the sensitivity of the recording apparatus, and the development of objective methods for calibrating the scale of electron energies[10,11] have enabled reliable and reproducible values to be obtained for the appearance potentials of negative ions and the effective yield of ions from electron–molecule interaction.

Several monographs[12-15] and reviews[16,17], dealing broadly with the problems of studying negative ions, have appeared recently. However, they do not devote much space to organic compounds, although the negative-ion mass spectrometry of organic compounds is acknowledged to be a promising and important trend.

The present Review examines published work on the dissociative capture of electrons by organic molecules with the formation of negative ions. It does not cover the large group of publications on the mass spectrometry of negative ions[18-25] in which the experimental technique of the traditional mass spectrometry of positive ions is imitated. While recognising the importance of this work, we must note that the ambiguity in interpreting processes leading to the formation of negative ions in these cases diminishes the theoretical value of the results and prevents their practical exploitation.

II. FORMATION OF NEGATIVE IONS. RESONANCES IN SCATTERING CROSS-SECTIONS OF ELECTRONS WITH MOLECULES

The main processes involved in the formation of negative ions by single collisions can be expressed

$$1)\quad AB + e \rightarrow (AB)^{*} + e \rightarrow A^{-} + B^{+} + e$$

$$2)\quad AB + e \rightarrow (AB)^{-} \rightarrow \begin{cases} \left.\begin{array}{l} A^{-} + B \\ B^{-} + A \end{array}\right. \text{(dissociative electron capture)} \\ \left.\begin{array}{ll} (AB)^{*} + e & \text{inelastic} \\ (AB) + e & \text{elastic} \end{array}\right\} \begin{array}{l} \text{electron} \\ \text{scattering} \end{array} \end{cases}$$

The first process consists in dissociation of a molecule, excited by electron impact, into two fragments with opposite charges. The dependence of the effective yield of ions on the energy of the electrons is the same as for the formation of positive ions, i.e. a smooth increase in yield with increase in energy from the threshold at which ions appear to a maximum (when the energy of the electrons exceeds the threshold by a factor of 3–4), which is followed by a slow decrease in yield.

The second process–capture of an electron by the molecule with formation of a short-lived negative molecular ion $(AB)^-$—is a resonance process occurring within a narrow range of electron energies (0.01–2 eV). If the law of the conservation of energy permits, the molecular ion may dissociate into negative splinter ions: i.e. dissociative capture of electrons takes place. If dissociation is impossible, the existence of the negative molecular ion ceases with the ejection of the electron (autoionisation), and elastic or inelastic resonance scattering of electrons is observed†. Autoionisation (autodetachment of an electron) always takes place, whether or not accompanied by dissociation of the negative molecular ion (dissociative electron capture), and in the former case competes with the latter process. The mean lifetime of the negative molecular ion with respect to autoionisation τ is a characteristic of the process of electron capture by a molecule.

The mechanism of establishment of the temporary bond between molecule and electron may be that on impact the electron loses its energy in the electronic excitation of the target molecule and finds itself in a bound state which has an energy below that of the excited state of the target. The electron cannot be detached while the molecule remains in an excited state; the lifetime of the resonant state is relatively long, 10^{-13}–10^{-14} s. Such resonances have been termed "electronically excited Feshbach resonances"[4].

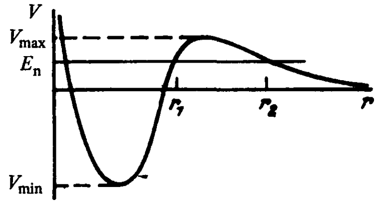

Figure 1. Typical interaction potential of electron and molecule (atom) for shape resonance: E_n is the energy of the trapped electron, and r_2–r_1 the range of effective action of the barrier.

Another mechanism for formation of temporary negative ions, without necessarily entailing excitation of the target molecule, involves the so called shape resonances (single-particle resonance, if electron capture takes place without excitation of the molecule, and electronically excited shape resonance). With shape resonance the bond between electron and molecule is established by the combined action of polarisation and exchange forces attracting the electron to the molecule and of the centrifugal force of repulsion when the incident electron possesses angular momentum relative to the target. The electron may be trapped in a quasi-discrete level of the potential well (Fig. 1) separated from the continuous spectrum by a centrifugal barrier. The reverse ejection of the electron takes place by tunnelling through the barrier. In contrast to Feshbach resonances, the parent state of the target has a lower energy, and ejection of the electron with transition of the molecule to the parent state (for the given resonance) is not energetically forbidden. The lifetime before autodetachment of the electron is determined for shape resonances by the width of the centrifugal barrier and the depth of the quasi-discrete level, and lasts 10^{-14}–10^{-15} s.

The so called vibrationally excited Feshbach resonance is due to electron capture at vibrationally excited levels of the molecular ion. If the electron affinity of the molecule is positive, the ground state of the negative molecular ion lies below that of the molecule. However, the vibrational energy of the negative ion can exceed the electron affinity of the molecule, and the vibrational levels of the ion will lie above the ground state of the molecule. An electron having positive energy may then be trapped at vibrationally excited levels of the ion. The kinetic energy of the electron is converted directly (without electronic excitation) into nuclear motion of the ion. Vibrationally excited Feshbach resonance is due to breakdown of the Born–Oppenheimer principle[4]. The lifetime before autoionisation of negative molecular ions formed with such resonance is extremely long in polyatomic molecules, reaching several tens of microseconds[15,16].

With vibrationally excited Feshbach resonance autoionisation of the negative ion may be prevented by a change in molecular configuration on conversion into the ion. A fairly long time would elapse before the configuration of the molecule–electron system would return to or approach the configuration before electron capture, from which autoionisation is possible.

Dissociative electron capture can thus be regarded as occurring in two stages: capture of an electron by a molecule with formation of a negative molecular ion (having a lifetime τ_a characteristic of a given process) is followed by dissociation along possible paths. According to O'Malley[3] the effective formation cross-section of negative ions in dissociative electron capture by diatomic molecules is given by the formula

$$\sigma = \mathrm{e}^{-\rho} C \frac{\Gamma_a}{\Gamma_d} \exp\left[\frac{{}^1\!/_2\Gamma_a^2 (E - E_0)^2}{{}^1\!/_4\Gamma_d^2}\right]; \quad \rho \approx \frac{\tau_d}{\tau_a},$$

where $\Gamma_a = \hbar/\tau_a$ is the so called autoionisation resonance width, τ_a the mean lifetime before autoionisation, Γ_d the observed width at mid-height on the peak effective yield of negative ions, τ_d the mean time of dissociation of the molecular ion into a negative ionic fragment and a neutral atom (radical), E the energy of the electron, E_0 the energy characteristic of the given process (closely similar to the energy corresponding to the maximum yield of ions), and $\hbar$ is Planck's constant.

This formula can be written $\sigma = \sigma_{cp}\mathrm{e}^{-\rho}$, where σ_{cp} is the cross-section for capture of the electron by the molecule and $\mathrm{e}^{-\rho}$ the probability of dissociation into a negative ion and a neutral fragment. The term $\mathrm{e}^{-\rho}$ is called the "survival factor", since it determines the proportion of molecular ions that have avoided autoionisation and have dissociated with the formation of stable (for the given experiment) negative ions. The dependence of τ_d on the reduced mass of the fragments that scatter on dissociation may be responsible for the so called isotope effect in

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† Reverting to the mass spectrometry of negative ions by the technique used for positive ions (fixed electron energy 50–70 eV, no control of the energy distribution of electrons in the ion source), we note that two processes—dissociative capture of electrons by molecules and the dissociation of molecules into ion-pairs—yield negative ions under these conditions. Dissociative capture takes place with electrons that have lost part of their energy in collisions with the walls of the ionisation chamber and with electrons produced by secondary emission. The relative contributions by these two processes to the ion current depend on the material and the design of the ionisation chamber, i.e. on the experimental conditions, which are difficult to standardise. This explains the poor reproducibility of the mass spectra of negative ions obtained in this way[18,19,26].

the measurement of the formation cross-section of negative ions[3,27]. However, Γ_d also depends on the reduced mass, and the change in ion-formation cross-section on isotopic substitution is determined not only by the survival factor[3,28,29].

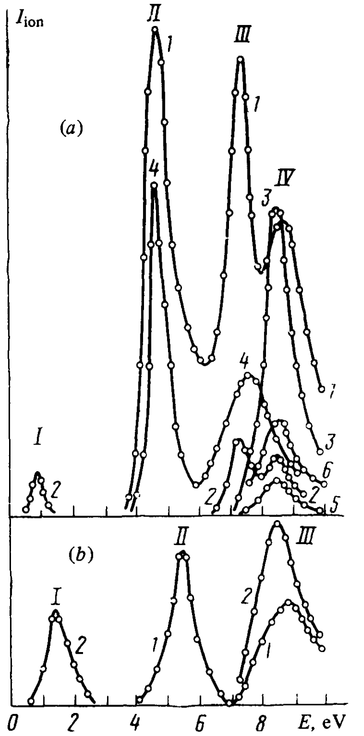


Figure 2. Curves of effective yields of negative ions for: (a) dimethyl sulphide: 1) S^-; 2) SCH_3^-; 3) SCH_2^-; 4) CH_3^-; 5) CH_2^-; 6) SH^-; and (b) di-isopropyl sulphide: 1) S^-; 2) $SC_3H_7^-$.

According to O'Malley[3] the above formula for σ is applicable also to polyatomic molecules, if all the quantities in it are assigned to separate normal vibrations of the molecule. A consequence of the multichannel breakdown of negatively charged polyatomic molecules is the formation of ions having different m/e ratios in the same resonance range of electron energies. While remaining within the same resonance region, the positions of the maximum yields of individual ions on the scale of electron energies $E_{\max}$ coincide neither with each other nor with the energy corresponding to maximum formation of the parent molecular ion. It follows from O'Malley's formula

$$E_{\max}=E_0-{}^1/_8\Gamma_d^2\left(\frac{d\rho}{dE}+\frac{1}{E}\right);\quad \frac{d\rho}{dE}>0$$

that $E_{\max}$ for each channel of formation of an ionic fragment depends on $d\rho/dE$, which in turn is determined by the direction of dissociation of the molecular ion ($\rho = \tau_d/\tau_a$).

Another reason for the difference in values of $E_{\max}$ for ionic fragments may be the formation of ions having different m/e ratios by consecutive decomposition of the type

$$(ABCD)^{\overset{\bullet}{-}} \xrightarrow{CD^{\dot{-}}} (AB)^{\overset{\bullet}{-}} \rightarrow A^- + B\ .$$

The AB^- ions are formed in a vibrationally excited state, and some of them, for which the energy of excitation exceeds the energy of the A–B bond, dissociate into A^- and B. With increase in the energy of the trapped electron (within the resonance range) the number of AB^- ions capable of dissociating increases: i.e. the maximum yield of A^- ions will shift to higher electron energies relative to the maximum yield of AB^- ions. This can be illustrated by the curves for the effective yield of $SC_3H_7^-$ and S^- ions from di-isopropyl sulphide[30] (Fig. 2); the latter ions are probably formed by the breakdown of excited $SC_3H_7^-$ ions. (Raising the temperature in the ionisation chamber, as would be expected, increases the yield of S^- ions.)

It is appropriate here to examine the energy balance of dissociative electron capture

$$AB + e \rightarrow (AB)^{\overset{\bullet}{-}} \rightarrow A^- + B\ .$$

Denoting the appearance potential of A^- ions by Aptl(A^-), the energy of dissociation of A–B by D(AB), and the electron affinity of an A atom (radical) by EA(A), we have

$$\text{Aptl}\ (A^-) = D\,(AB) + EA\,(A) + \varepsilon_{tr} + \varepsilon_{ie}$$

where ϵ_{tr} is the translational energy of the reaction products and ϵ_{ie} the energy of internal excitation of the fragments. The corresponding expression for B^- is

$$\text{Aptl}\ (B^-) = D\,(AB) + EA\,(B) + \varepsilon'_{tr} + \varepsilon'_{ie}).$$

In a series of papers Franklin et al.[31-33] obtained a formula linking the mean translational energy $\bar{\epsilon}_{tr} = \epsilon^*/\alpha N$ with the excess energy ϵ^* (the energy exceeding the threshold for dissociative electron capture: $\epsilon^* = \epsilon_{tr} + \epsilon_{ie}$) and the number of vibrational degrees of freedom of the molecule N, in which α is a semi-empirical parameter having the value 0.42 for such processes.

The chief experimental methods for studying resonances in the scattering of electrons by molecules are currently electron-impact spectroscopy and the mass-spectrometric investigation of resonant processes in the formation of negative ions. The former is characterised by relatively high energy-resolving power, which ensures accurate determination of the position of resonant levels and the possibility of recording short-lived negative molecular ions. The variety of experimental methods in electron-impact spectroscopy (each of which has its advantages) can be regarded as a virtue, permitting a flexible approach to solving a problem. Information on the energy levels of atoms or molecules is obtained by analysing the changes in momentum and energy of electrons in single collisions between electrons in the primary beam and atoms or molecules. A review has been published on electron-impact spectroscopy[7].

Negative-ion mass spectrometry involves a more reproducible technique: the rigid requirements of mass spectrometry do not permit wide variation in the design of the ion source or the experimental conditions. However, the mass analysis of the ionic fragments and the absence of a background of potential scattering (only resonance processes are recorded) make it possible to examine resonance phenomena in the interaction of electrons with complex molecules, as yet inaccessible to electron-impact spectroscopy.

Experimental procedure in mass-spectrometric investigations has been described repeatedly in reviews and monographs[12-17,34]. Study of dissociative electron capture by recording negative ions is undertaken with the usual mass spectrometers (static or time-of-flight). Changing to the registration of oppositely charged ions for the investigation of dissociative electron capture requires, of course, not only simple reversal of fields (electric and magnetic), but also several design modifications of the ion source (connected mainly with the need to monochromatise the electron beam and calibrate the electron-energy scale), and the sensitivity of the instrument must be improved. However, the conversion of commercial mass spectrometers into instruments suitable for investigating dissociative electron capture by molecules with the formation of negative ions is technically not a complicated task[11,35,36].

III. DISSOCIATIVE CAPTURE OF ELECTRONS BY ORGANIC MOLECULES

The studies considered in the present Section are not all equivalent with respect to the experimental technique used. Different workers employed apparatus of different sensitivities; different reference points were used for calibrating the electron-energy scale; and the energy distribution of the electrons was not strictly the same. In several studies attention was paid mainly to measuring the appearance potentials of the negative ions, without determining the positions of the maximum yields of ions on the electron-energy scale; in other cases the efficiency of the emission of ions was not determined[37,38]. Despite the differences in experimental technique, however, the values cited in the present Section from various publications are mutually comparable. The deviations (±0.2–0.3 eV for the positions of the resonance peaks on the energy scale, and ±20% for the relative intensities of the ions) are not so significant as to support the currently held view that data on dissociative electron capture by molecules show poor reproducibility[39-42].

1. Alkanes

Several papers have been published on dissociative electron capture by alkane molecules[37,39,43-45]. Methane exhibits two peaks representing the formation of ions having appearance potentials of 8.3 eV (H^-, CH_2^-) and 9.3–9.6 eV (H^-, CH^-, CH_2^-). Two peaks have been observed with ethane (8.3 and 9.2 eV), whereas the spectra of propane, n-butane, and isobutane contain one resonance peak corresponding to the formation of ions having appearance potentials of 7.6–7.8, 7.8, and 7.4–7.5 eV respectively[39]. The greatest probability of formation is found with H^- ions ($\sigma \simeq 10^{-19}$ cm^2). A comparatively large formation cross-section was noted for the ions CH_2^- and CH^- ($\sim 10^{-19}$ and $\sim 10^{-20}$ cm^2) from methane, CH_2^- from ethane, and CH_3^- from propane and isobutane ($\sim 10^{-20}$ cm^2). The formation cross-sections of C_2H^-, $C_2H_3^-$, and CH_4^- ions are of the order 10^{-21}–10^{-22} cm^2.[39]

In the spectrum of tetradeuteromethane the probability of formation of D^- ions is greater, while that of CD_2^- ions is smaller than those of the corresponding processes in methane[45,46]. The ratios of the formation cross-sections are $\sigma(H^-)/\sigma(D^-) = 0.8$ and $\sigma(CH_2^-)/\sigma(CD_2^-) = 25$.

2. Alkenes, Polyenes, and Alkynes

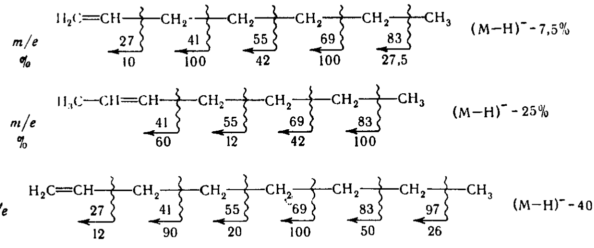
The effective-yield curves for negative ions resulting from the interaction of electrons with ethylene, propene, and isobutene molecules[39] indicate the existence of two resonance peaks of electron capture in the range of electron energies 7–13 eV. The ion-formation cross-section does not exceed 10^{-19} cm^2 in ethylene and isobutene, and 10^{-20} cm^2 in propene and but-1-ene (Table 1). The energy of excitation of the first Rydberg state ($^1B_{3u}$) of the ethylene molecules is 7.25 eV,[47] and peaks of negative ions from dissociative electron capture in ethylene can be assigned to the decomposition of $C_2H_4^-$ ions, which are formed by a mechanism of Feshbach resonances of Rydberg states of the molecules. The lowest state of the $C_2H_4^-$ ion recorded by transmitted-electron spectroscopy is responsible for the peak of resonant scattering of electrons with its maximum at 1.76 eV.[48] A molecular ion in this state breaks down without dissociation into ionic fragments. In propene a small peak due to C_2H^- ions (cross-section 10^{-21} cm^2) has been recorded with its maximum at 3.8 eV.[39]

Table 1. Appearance potentials (Aptl) of ions and their intensities*.

Ethylene			Propene			Isobutene		
ion	intensity	Aptl ± 0.3, eV	ion	intensity	Aptl ± 0.3, eV	ion	intensity	Aptl ± 0.3, eV
H^-	430	7.6;9.7	H^-	325	7.7	H^-	585	7.8
CH^-	174	7.3;8.7	CH_2^-	48	6.1;7.3; 7.8	CH^-	43.5	7.9
CH_2^-	131	8.8	CH_3^-	20	—	CH_2^-	130	7.8
C_2^-	60	10.4	C_2H^-	77	2.6;6.3; 7.6	CH_3^-	57.5	7.4
C_2H^-	520	7.1;10,0	$C_3H_3^-$	18	—	$C_3H_3^-$	58	5.8;7.6
$C_2H_3^-$	19.8	—	$C_3H_5^-$	250	5.9;7.6	—	—	—

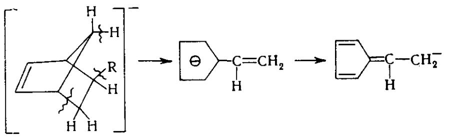
* Unit intensity corresponds to $\sigma = 10^{-22}$ cm^2.

The dissociative electron-capture mass spectra of hept-1-ene, hept-2-ene, and oct-1-ene are given below as schemes representing the rupture of the negative molecular ions together with the relative intensities at maximum effective yields of the ions, which correspond to electron-energies of ~8 eV:



These show that formation of ions is a consequence of the rupture of carbon–carbon bonds with addition of the electron to the fragment containing the double bond. However, the absolute formation cross-sections of the ions are small ($\sim 10^{-21}$ cm^2).[49]

Among 5-substituted bicyclo[2,2,1]heptene derivatives norbornene itself and 5-methylnorbornene have the simplest spectra[50,51], with three resonance peaks due to formation of the cyclopentadienyl anion $C_5H_5^-$ and one peak due to each of the ions $C_7H_7^-$, $C_4H_3^-$, and $(M - H)^-$. Formation of the $C_5H_5^-$ ion can be attributed to retrodiene decomposition, whereas the $C_7H_7^-$ ion is formed by the simultaneous rupture of carbon–hydrogen and carbon–carbon bonds:



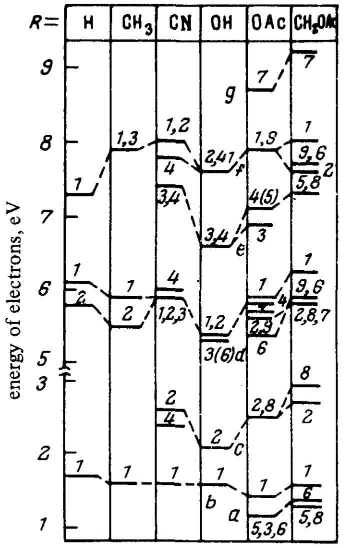


Figure 3. Positions of maximum effective yields of negative ions on scale of electron energies for interaction of electrons with norbornene and its 6-substituted derivatives: 1) $C_5H_5^-$; 2) $(M-H)^-$; 3) $RC_2H_2^-$; 4) R^-; 5) $COOCH_3^-$; 6) $COCH_3^-$; 7) C_2HO^-; 8) $(M - Ac)$; 9) $(M - OAc)$.

The process of lowest energy—emission of $C_5H_5^-$ ions at 1.6–1.7 eV—corresponds to the trapping of an electron in the first vacant π^* orbital. A second maximum, at 5.6–5.8 eV, can be assigned to Feshbach resonance involving the first triplet state of the molecules. The third peak, at 7.2–7.3 eV, is due to Feshbach resonance with excitation of Rydberg states of the molecule. Fig. 3 shows that the positions of maximum emission of ions vary with the substituent. For example, the low-energy peaks due to ions having m/e = 59.43 (levels *a*) are present in the spectra of molecules containing a CH_3COO group. The *a* level implies a single-particle resonance involving the lowest unoccupied orbital localised on the acetoxyl group. Levels *c* and *e* can be attributed to electron capture with $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ excitation: they are observed when the substituent contains a heteroatom with a lone pair of electrons. Thus data on the fragmentation of the negative molecular ions supplements the spectral characterisation of the molecule over a wide energy range.

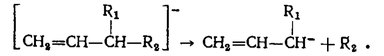
Molecules of polyenes—5-methylhepta-1,3,6-triene, octa-1,3,7-triene, 6-methylnona-2,4,7-triene, 9-methylundeca-1,3,7,10-tetraene, and 3,8-dimethyldeca-1,4,6,9-tetraene—form negative ions on interaction with slow electrons, with three ranges of electron energies in which the trapping of electrons is followed by dissociation of the negative molecular ion[52,53]. The first two ranges, corresponding to maximum effective yields of ions at 2.5 and 6 eV, consist of three mass lines due to C_2H^- (m/e = 25), or $(M - H)^-$, and $(M - C_2H_3)^-$ ions, whereas in the third range, in which the maximum effective yields are grouped around 8 eV, the mass spectrum comprises six lines. The effective formation cross-section of ions corresponding to the maximum intensity is $\sim 10^{-20}$ cm^2.

It is significant that negative ions are formed predominantly by the simple rupture of bonds, without the rearrangements inherent in the breakdown of positive ions. As a consequence, the spectra of structural isomers are sharply differentiated, as is evident in the mass spectra of 5-methylhepta-1,3,6-triene and octa-1,3,7-triene (Table 2).

Table 2. Values of m/e and relative intensities (% of I_{max}) in mass spectra of negative ions of trienes.

m/e	107	81	67	55	53	51	41	27	25
5-Methylhepta-1,3,6-triene	28	76	—	42	100	80	14	57	80
Octa-1,3,7-triene	15	—	100	—	40	13	20	—	20

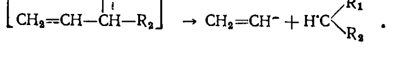
The formation of negative ions was interpreted as σ–π^* excitation with capture of the extra electron in an antibonding σ^*-orbital. This accompanied by β-cleavage relative to the double bond with retention of the negative charge on the fragment. Two electrons in σ^*- and π^*-orbitals form a new π^2-orbital of the negative ion, while the electron of the σ-orbital becomes a σ-electron of the neutral fragment:



$$\left[CH_2{=}CH{-}\overset{\overset{\displaystyle R_1}{|}}{C}H{-}R_2\right]^- \rightarrow CH_2{=}CH{-}\overset{\overset{\displaystyle R_1}{|}}{C}H^- + R_2\,.$$

$$\sigma\pi^*\sigma^* \rightarrow (\pi^2) + \sigma$$

Such a process corresponds to ions of m/e 81 and 55 in the spectrum of 5-methylhepta-1,3,6-triene, and to ions 41 and 67 in that of octa-1,3,7-triene. The $\sigma\pi^*\sigma^*$-state of a negative molecular ion may lead to α-cleavage, when the negative charge will be concentrated on the fragment containing the double bond:

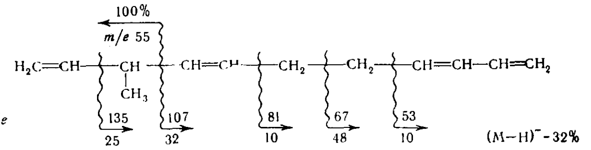


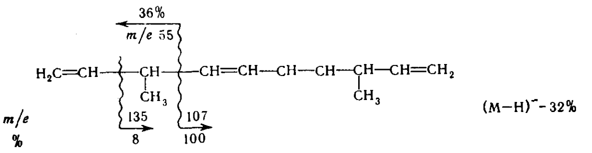
$$\left[CH_2{=}CH{-}\overset{\overset{\displaystyle R_1}{|}}{C}H{-}R_2\right]^- \rightarrow CH_2{=}CH^- + H^{\cdot}C\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\,.$$

$$\sigma\pi^*\sigma^* \rightarrow (\sigma^2) + \pi$$

In the spectra of these trienes such cleavage corresponds to intense ions having *m/e* 53. In addition to the ions formed by α- and β-rupture, dissociation of a carbon–carbon bond with detachment of two hydrogen atoms results in ions with *m/e* 107, 51, and 25—$(M - H)^-$, $C_4H_3^-$, and C_2H^-. The intensity of the rearranged 41 peak in the spectrum of the methylheptatriene is low. The 67 peak is absent, although quite intense in the spectrum of the octatriene, whereas the latter contains no peak at 55. The corresponding ions cannot be formed by simple rupture of carbon–carbon bonds. The absence of an 81 peak from the spectrum of the octatriene is due to the fact that this fragment cannot be formed by either α- or β-cleavage: it would require either γ-rupture or α-rupture with transfer of the extra electron to the $\cdot CHR^1{-}R^2$ fragment, which obviously does not occur.

Three resonance ion-emission peaks are observed in dissociative electron capture by 9-methylundeca-1,3,7,10-tetraene and 3,8-dimethyldeca-1,4,6,9-tetraene. Their mass spectra can be represented by a scheme of α- and β-cleavage with the mass number and relative intensities (as percentages of the maximum intensity):





A characteristic feature of the spectra of negative ions of polyenes is the necessary presence of fragments containing an intact system of conjugated double bonds.

Fig. 4 shows the mass spectra of positive and negative ions of isomeric tetraenes. It is very significant that the slight differences in the mass spectra of positive ions of isomers bear no clear relation to the structure of the molecules. As a consequence, mass spectra cannot be used to assign a test material to a particular isomeric form. On the other hand, the mass spectra of negative ions resulting from dissociative electron capture by polyenes enable the structural formula to be determined without the use of other information.

Among compounds containing a triple bond only acetylene and propyne have been investigated. Their spectra reveal a large formation cross-section for $(M - H)^-$ ions ($\sim 10^{-18}$ cm^2).[37,39,44,53,54]

3. Benzene and its Derivatives

Electron-impact spectroscopy indicates[48,55,56] the capture of electrons by benzene molecules in the lowest unoccupied π^*-orbital (single-particle resonance, $^2E_{1u}$ state of $C_6H_6^-$) with electrons of energy 1.2–1.7 eV (various authors give differing values). The average lifetime of $^2\Sigma_{1u}C_6H_6^-$ ions is short ($<10^{-6}$ s), and the ions do not appear in the mass-spectrometric investigation of benzene. Sanché and Schulz[48] observed an additional peak, in the range 4–6 eV in the spectrum of electrons scattered by benzene molecules, and ascribed it to the capture of electrons in a b_{2g}-orbital of the molecule. Negative ions are not observed in this range of electron energies, although dissociation of $C_6H_6^-$ with the formation e.g. of $C_6H_5^-$ ions is energetically possible. Resonance peaks of negative ions are recorded at electron energies of 7–12 eV.[39,40]

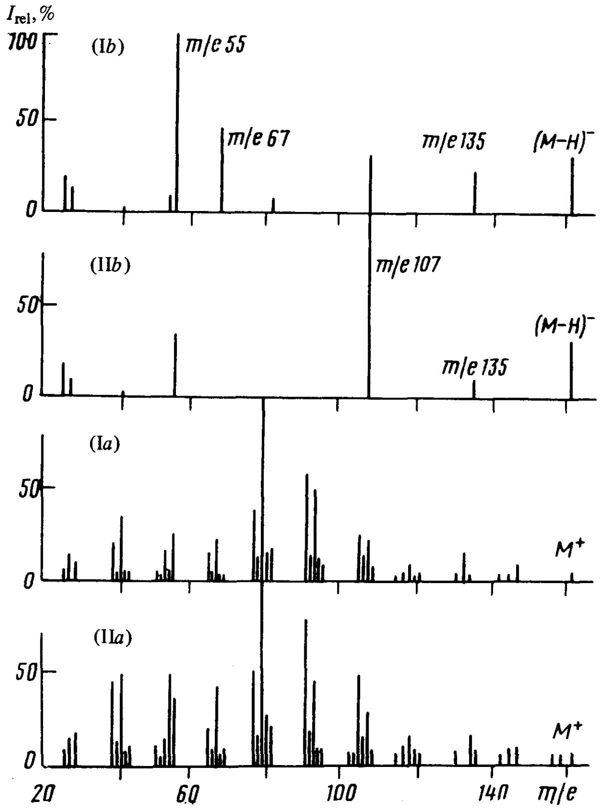


Figure 4. Mass spectra of: *a*) positive ions; *b*) negative ions of: I) 9-methylundeca-1,3,7,10-tetraene; II) 3,8-dimethyldeca-1,4,6,9-tetraene.

Table 3. Effective yields of negative ions (at maximum emissions of ions)*.[40]

Ion	Benzene	Toluene	Ethyl-benzene	Isopropyl-benzene	Butylbenzenes n-	s-	t-
$(M-H)^-$	100	46	24	23	41	22.2	15.7
$(M-2H)^-$	0.25	11	—	—	—	—	—
$(M-3H)^-$	1.1	0.3	2.0	—	2.0	—	—
$C_8H_9^-$	—	—	—	0.3	—	20	5.7
$C_8H_7^-$	—	—	—	4.6	2.2	—	0.3
$C_7H_7^-$	—	$(M-H)^-$	0,37	—	34	210	0.35
$C_6H_5^-$	$(M-H)^-$	0.9	6.7	21.6	6.1	15	70
$C_5H_5^-$	1.3	0.55	—	—	—	—	—
$C_4H_3^-$	7.8	0.74	—	—	—	—	—
C_2H^-	80	9.0	0.6	20.5	10.5	12	21
C_2^-	1.4	2.2	—	—	—	—	—
CH_3^-	—	—	—	—	—	—	52

* Unit intensity corresponds to $\sigma = 10^{-21}$ cm^2.

Table 3 shows that the main process in dissociative electron capture by benzene molecules is detachment of a hydrogen atom with localisation of the electron on the phenyl radical ($\sigma \simeq 10^{-19}$ cm^2 [39]). Formation of C_2H^- ions has a similar cross-section, whereas the effective yield of $C_2H_5^-$, $C_4H_3^-$, and C_2^- ions is one-tenth of this.

The minimum energy for the reaction $C_6H_6 + e \rightarrow C_6H_5^- + H$ to occur is 2.2 eV on the assumption that the electron affinity of the $C_6H_5^{\bullet}$ radical is 2.2 eV [57] and the energy of rupture of a carbon–hydrogen bond in benzene is $D(C_6H_5{-}H) = 4.4$ eV.[58] At the maximum yield of $C_6H_5^-$ ions (8 eV) the excess energy $E^* = 5.8$ eV is distributed between internal excitation of the $C_6H_5^-$ ion and translational energy of the reaction products. According to Franklin's formula $\bar{\epsilon}_{tr} = 5.8/0.42 \times 30 = 0.45$ eV, so that the total store of vibrational energy of the $C_6H_5^-$ ion is ~5.4 eV, which is 3.2 eV greater than the electron affinity of $C_6H_5^{\bullet}$. Even regarding this formula as a very crude approximation and bearing in mind the large excess energy of formation of the ion, we may conclude that $C_6H_5^-$ ions are formed in an autoionised state, i.e. with a sufficient store of vibrational energy for detachment of an electron.

Direct proof of the instability of $C_6H_5^-$ ions with respect to ejection of an electron has been obtained[59, 60] by measuring the mean lifetimes τ with respect to autoionisation of $C_6H_5^-$ ions from C_6H_6 and of $C_6D_5^-$ ions from C_6D_6 as respectively 47 ± 5 and 37 ± 5 μs. The effect of isotopic substitution on τ is probably due to a change in the overlap of the atomic vibrational wave-functions of the ion and of the corresponding neutral radical when hydrogen atoms are replaced by deuterium atoms. The C_2H^- ions were stable, which was not surprising, since their formation involved a lower excess energy, and part of the vibrational energy was associated with the neutral fragment. Two values were obtained for the isotope effect in the formation cross-section of the ions: $\sigma(C_6H_5^-)/\sigma(C_6D_5^-) = 1.18$ [61] and 5.4.[59] It is difficult to explain such a marked discrepancy, far exceeding possible experimental errors, but later work may reveal its cause.

Alkylbenzenes form negative ions[40] in the same range of electron energies as with benzene, though the maximum effective yields are slightly displaced (up to 0.3 eV) to higher energies. The maximum peaks in the dissociative electron-capture mass spectra of s- and t-butylbenzenes correspond to the ions $C_7H_7^-$ and $C_6H_5^-$ respectively. With the other alkylbenzenes investigated, the formation of $(M - H)^-$ ions is the most probable. The presence of an alkyl substituent changes the ways in which the molecular ion breaks down: thus $C_5H_5^-$, $C_5H_4^-$, $C_4H_3^-$, and $C_4H_2^-$ ions are present only in the mass spectra of benzene and toluene, but in alkylated benzenes both the formation cross-section of $(M - H)^-$ and C_2H^- ions and the total ion current at the maximum effective yield of ions have diminished. The latter does not apply to s-butylbenzene, with which the total ion current is increased by the large cross-section for formation of $C_7H_7^-$ ions, which exceeds that of $(M - H)^-$ ions from benzene by a factor of 2.1.

Study of dissociative electron capture by certain monosubstituted benzene derivatives has shown[51] ion-formation cross-sections of $\sim 10^{-19}$ cm^2, with the main processes of dissociation of the molecular ion coinciding with those in alkylbenzenes. The molecules C_6H_5X and C_6H_4XY, where X and Y respresent substituents possessing high electron affinities, exhibit effective cross-sections of dissociative electron capture larger by factors of 10^2–10^3, with several electron-capture resonance peaks. In chlorobenzene and bromobenzene the first peak with formation of halide ions is located at 0.6 eV; the capture of thermal electrons by iodobenzene molecules results in the appearance of iodide ions[62–64].

A long-lived negative molecular ion ($\tau = 40$ μs; energy of electrons ~0 eV) has been recorded in nitrobenzene[5]. The first peak in the electron-energy range 1–2 eV represents NO_2^- and $C_6H_5^-$ ions ($\sigma \simeq 2 \times 10^{-16}$ and 10^{-19} cm^2 respectively).[64, 65] Maximum yields of the ions— NO_2^- ($\sigma = 2 \times 10^{-16}$ cm^2), $C_6H_5NO^-$ (3×10^{-19}), $C_6H_4NO_2^-$ (2.5×10^{-18}), $C_6H_5^-$ (1.2×10^{-18}), CN^- (1.3×10^{-18}), NO^- (6×10^{-20}), $C_6H_5N^-$ (1.2×10^{-18}), and $m/e = 43, 42, 41$ (10^{-18} cm^2)—are obtained with electrons of energy 4 eV. Furthermore, peaks due to O^-, C_2H^-, and m/e 92 are situated with their maximum at 5 eV, and to OH^-, C_2H^-, and $(M - H)^-$ ions at 7 eV (cross-section $\sim 10^{-19}$ cm^2).

Two resonance peaks due to NO_2^- ions were observed in *o*- and *m*-nitrotoluenes[64]. It is interesting that the two peaks are of equal intensity in the *ortho*-isomer, but in *m*-nitrotoluene the intensity of the first peak with its maximum at 1.1 eV is only 15% of that of the second peak (maximum at ~3.3 eV). The energy of the resonant states has diminished by 0.3 eV in *o*-nitrotoluene. Molecular ions of *m*-chloronitrobenzene and *m*-iodonitrobenzene decompose along two channels with the emission of NO_2^-, Cl^-, and I^- ions[66]. In benzonitrile not only the molecular ion ($\tau \simeq 5$ μs) but also CN^- ions (two peaks) are observed with peaks due to $C_6H_4^-$ and $C_6H_4CN^-$ ions.

4. Fused-ring Aromatic Hydrocarbons

The only ionic fragment formed in naphthalene, fluorene, anthracene, and phenanthrene results from detachment of a single hydrogen atom from the negative molecular ion. Maxima on the effective-yield curves of $(M - H)^-$ ions from naphthalene and fluorene coincide with the corresponding maximum for benzene, but dissociative electron capture takes place over a wider range of electron energies than does the formation of $C_6H_5^-$ ions from benzene. Interaction of electrons with fluorene molecules gives rise to a further process of formation of $(M - H)^-$ ions with a maximum at 1.6 eV, which has been regarded[67] as corresponding to formation of a fluorenyl anion.

It is interesting that the dissociative electron-capture spectra of anthracene and phenanthrene are different. The effective-yield curve for $(M - H)^-$ ions from anthracene exhibits an inflexion, which is less strongly marked with phenanthrene. Furthermore, non-dissociative capture of electrons (having energies close to zero) is observed in anthracene. As a result, a negative molecular ion of anthracene is formed with a finite lifetime with respect to autoionisation ($\tau = 21$ μs). The formation cross-section of $(M - H)^-$ ions from anthracene and phenanthrene is $\sim 10^{-17}$ cm^2, and the cross-section of non-dissociative electron capture by anthracene molecules is 10^{-16} cm^2. Hence negative-ion mass spectrometry may be used to detect anthracene present as impurity (up to 0.5%) in other compounds, including phenanthrene.

5. Cyclopentadiene and Metallocenes

On interaction with electrons cyclopentadiene loses a hydrogen atom and is converted into a stable $C_5H_5^-$ anion, with a maximum probability for electrons of energy 2.05 eV.[41] A further resonance process is observed at 8 eV, leading to the formation of $C_5H_5^-$, $C_5H_4^-$, $C_5H_3^-$, $C_3H_3^-$, and

C_2H^- ions with respective intensities of 3.6%, 1.6%, 1.2%, 11%, and 20.5%. At 2.05 eV the intensity of the $C_5H_5^-$ peak reaches 100%.[41]

In dissociative electron capture by ferrocene, cobaltocene, manganocene, and nickelocene molecules[68] $C_5H_5^-$ ions are formed in the range of electron energies 0.5–1.0 eV, with widely varying formation cross-sections. Ferrocene and cobaltocene have the smallest cross-section (3×10^{-21} cm^2), that of nickelocene is larger by a factor of 25, and manganocene occupies an intermediate position. The effective formation cross-section for $C_5H_5^-$ ions is relatively small, that of $C_5H_5Co^-$ ions (at 0.7 eV) is 1.8×10^{-20} cm^2, and the non-dissociative capture cross-section of thermal electrons with formation of $CoC_{10}H_{10}^-$ ions is 6×10^{-18} cm^2.

Study of dissociative electron capture by dicyclopentadienyl dichlorides $M(C_5H_5)_2Cl_2$, where M = Ti, Zr, Hf, revealed in all cases the formation of molecular ions by the capture of thermal electrons, the probability of ion formation being greater the heavier the metal M.[69]

6. Five-membered Heterocycles

Five-membered heterocycles form negative ions in two ranges of electron energies, in both of which the mass spectrum contains a relatively large number of lines[41,70]. An exception is pyrrole, with which only $(M - H)^-$ ions are observed in the first, low-energy range. Table 4 reveals greater fragmentation of molecular ions in the second than in the first range, with an increase in the relative probabilities of formation of ions having low *m/e* values and a decrease in the yield of $(M - H)^-$ ions. The isotope effect in the cross-section for formation of the latter ions from thiophen is 1.4 and 12.1 in the first and second resonance peaks. In both resonance regions these $(M - H)^-$ ions are in autoionisation states, with $\tau(SC_4H_3^-)$ = 240 and 220 μs respectively.

Table 4. Effective yields of negative ions in two resonance peaks of selenophen, thiophen, furan, and pyrrole*.[26,70,41]

X Electrons, eV	Se 4.9–5.3	S 5.3–5.7	O 5.5	Se^{II} 7.8–8.1	S^{II} 8.3–8.5	O^{II} 9.8–10	NH^{II} 8.9–10.2
$XC_4H_3^-$	220	144	53	2.1	79	8.7	160
XC_2H^-	100	100	80	336	650	19.3	81.5
XH^-	195	157	0.1	63	136	0.2	—
X^-	320	130	—	2400	87	—	—
C_4H^-	0.4	14.4	10	61	150	3	—
$C_3H_3^-$	—	—	22.2	—	11.5	3.7	153
C_2H^-	5.5	8.5	18.7	83	100	2.5	—

* Unit intensity corresponds to $\sigma = 10^{-21}$ cm^2.

Differences between the dissociation of negative molecular ions in the first and second ranges of electron capture have been examined[26] on α-deuterated thiophen and selenophen. It was found that $(M - H)^-$ ions of the first peak were formed by the detachment of either an α- or a β-hydrogen atom, with relative probabilities of 1 : 3. The same relative probabilities applied to the formation of C_2H^- ions.

In thiophen the decomposition channels of the molecular ion with formation of $(M - H)^-$ and SC_2H^- are independent in the sense that the degradation $(M - H)^- \rightarrow SC_2H^-$ does not take place. An isotope effect is observed in the formation cross-section of $(M - H)^-$ ions, but the yield of SC_2H^- ions is almost unaffected by deuteriation of the molecule[59]. Formation of SH^- ions takes place almost exclusively by migration of hydrogen atoms from the β-position. In the second peak the formation of $(M - H)^-$ and SC_2H^- ions also corresponds to two processes, involving detachment of hydrogen atoms from α- and β-positions, but the relative probabilities of the two processes are about the same as with the first peak.

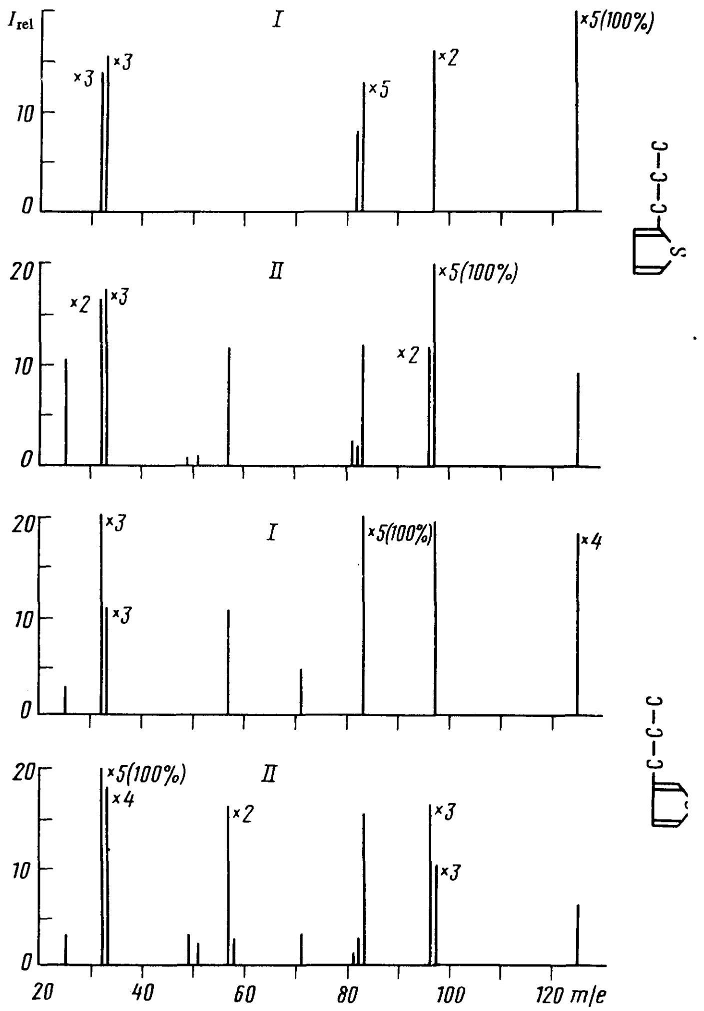
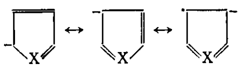


Figure 5. Mass spectra of negative ions of 2- and 3-propylthiophens: I) first range of electron capture (electrons of energy ~5 eV); II) second range (~8 eV).

Breakdown of alkylthiophen molecular ions of the first peak (maximum yields of ions at ~5 eV) is closely similar to that of the corresponding molecular ion of thiophen. Substitution has little effect on the modes of decomposition of the molecular ion. For example, detachment of alkyl radicals from a β-position is more probable than the detachment of α-substituents, and the relative probabilities of formation of $(M - H)^-$, H^-, and C_2H^- ions in α- and β-alkylated thiophens can easily be interpreted qualitatively in terms of the relative probabilities of different modes of dissociation of the molecular ion of thiophen. In the second peak substitution has a more significant effect on the breakdown of molecular ions, which is apparent in the absence of consistency in the relative probabilities of individual modes of dissociation of molecular ions of thiophen and of alkylthiophens (Fig. 5).

While dissociative electron capture by five-membered heterocycles shows a general similarity, the most closely similar processes evidently occur with selenophen and thiophen. Formation of ions of the heteroatom does not occur in furan, although O^- ions are readily formed with other oxygen-containing compounds, and the line due to hydroxide ions is weak. Pyrrole does not exhibit NH^- ions at all. The vacant *d*-orbitals of sulphur and selenium enable the structures



to be included among those of the negative molecular ion. Such structures are impossible with furan and pyrrole. They are probably responsible for formation of the X^-, XH^-, XCH^-, and XC^- ions characteristic of thiophen and selenophen but absent from the dissociative electron-capture spectra of other five-membered heterocycles.

With indole and several alkylindoles the only negative ions that could be observed were $(M - H)^-$. Breakdown of the benzene ring, as found in fused aromatic hydrocarbons, does not occur on electron capture. The maximum effective yields of these ions from indole and 2,3,7-trimethylindole occur with electron energies of 1.55 and 1.65 eV respectively. Substitution at the nitrogen atom, as e.g. in 1,2,3,7-tetramethylindole and 1,7-propanoindole, eliminates this low-energy resonance formation of ions. From this it was deduced[41] that $(M - H)^-$ ions are formed from indole and from 2,3,7-trimethylindole as a result of rupture of the nitrogen–hydrogen bond.

7. Pyridines and their *N*-Oxides

The scattering of electrons by pyridine molecules reveals two states of short-lived molecular ions at electron energies of 1.2 and 1.6 eV,[71] or 0.84 and 1.3 eV according to other workers[56]. Single-particle shape resonances are probably involved, corresponding to electron capture at vacant π-orbitals of the molecule. Study of dissociative electron capture by pyridine and alkylpyridines[40] showed that, in contrast to benzene and alkylbenzenes, the two states of negative molecular ions break down with the formation of negative ionic fragments. The first resonance peak of ionic emission with maxima at ~4.5–4.6 eV corresponds to NC_3^-, C_2H^-, C_2^-, and in pyridine also $NC_5H_4^-$ ions. The mass spectrum of the second peak (at ~8 eV) contains more lines, and the modes of dissociation of the molecular ion are largely similar to those for benzene, only a large relative probability of formation of ions with destruction of the ring is observed (such ions as $^-N{:}CH.C{\vdots}CH$ and $^-N{:}C{:}CH_2$).

The isotope effect in the formation cross-section of $(M - H)^-$ ions from pyridine in the second peak is also closely similar to that in benzene: $\sigma(NC_5H_4^-)/\sigma(NC_5D_4^-) = 6 \pm 0.5$. The isotope effect is smaller in the first peak (3.1 ± 0.5). The probable reason is the shorter mean lifetime with respect to autoionisation of the molecular ion of pyridine produced by trapped electrons of energy 8 eV than by those of energy 4.5 eV. The $(M - H)^-$ ions are formed in an autoionised state, with $\tau(NC_5H_4^-) = 60$ μs (8 eV) but $\tau(NC_5D_4^-) = 68$ μs (8 eV): i.e. deuteriation increases the lifetime, in contrast to the case of benzene[60].

The Reviewers have investigated the mass spectra of the *N*-oxides of pyridine and of the three isomeric alkylpyridines. The oxygen atom has a substantial effect on processes involved in the dissociative capture of electrons, resulting both in the appearance of new excited states of the negative molecular ions and in a change in the possible channels of decomposition of the molecular ions. Five main states of excited molecular ions, denoted *a–e*, were distinguished by the positions of the maximum effective yields of ions on the electron-energy scale and by the modes of decomposition. The low-energy state *a* was represented in the spectrum of pyridine *N*-oxide by lines due to the ionic fragments $(M - H)^-$, $NC_3H_3^-$, $NC_3H_2^-$, and NC_3^-, with peaks of relatively low intensities, while the maximum efficiency of formation is observed with electrons of energy 0.2–0.5 eV.

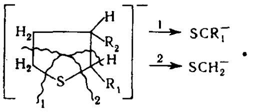
Molecular ions in state *b* break down with ejection of a C_2H_3 fragment (ions with *m/e* 68). The maximum of the resonance peak on the emission curve of $(M - C_2H_3)^-$ ions is located at 0.8 eV. The most intense peaks in the spectrum of pyridine *N*-oxide are due to ions formed by the dissociation of ions in state *c*, the maximum yield being observed at 3–3.2 eV. The breakdown of molecular ions in this state is represented by peaks due to $(M - H)^-$, $(M - OH)^-$, $(M - OCH)^-$, O^-, OH^-, and ions with $m/e = 64$. State *d* of molecular ions is apparent from the effective-yield curves for O^- ions, which show two poorly resolved peaks: the first (at 3.2 eV) corresponds to state *c*; the second peak (at 4 eV) indicates the existence of yet another state of molecular ions decomposing with the emission of O^-. Decomposition of molecular ions in the high-energy state *e* gives a mass spectrum rich in peaks, although their relative intensities are comparatively low. Besides the purely "pyridine" ions $NC_3H_2^-$, NC_3H^-, $NC_2H_2^-$, NC_2H^-, and C_2H^-, the fragments $(M - OH)^-$, $(M - CO)^-$, $(M - CHO)^-$, O^-, and OH^- are observed, as well as ions having *m/e* ratios of 41, 42, 49, and 68, whose maxima occur in the range of electron energies 8–9 eV. Replacement of hydrogen by methyl does not give rise to new states of the negative molecular ions, only some redistribution of the probabilities of different decomposition channels.

8. Sulphides

Sanché and Schulz[48] studied hydrogen sulphide molecules by transmitted-electron spectroscopy, and with electrons of energy 2 eV observed shape resonance (single-particle resonance) corresponding to capture of electrons in the lowest unoccupied $4a_1$ orbital of the molecules. Electronically excited Feshbach resonance with excitation of the lone pair of electrons on the sulphur atom takes place when the electron energy reaches ~4 eV. In the range of electron energies ⩾8 eV resonant states of H_2S^- are observed with two Rydberg electrons. The positive molecular ion H_2S^+ is the grandparent state for such states of negative ions.

Studies have been made[73-75] on dissociative electron capture by a large group of aliphatic sulphides, disulphides, and thiols. Fig. 2 illustrates effective-yield curves for negative ions of dimethyl sulphide. The resonance peaks of ion emission are denoted by Roman numerals in order of increasing energy. Peak (I) represents only SCH_3^- ions, the peak (II) CH_3^- and S^- ions. If peak (I) is assigned to single-particle resonance, and peak (II) to electronically excited Feshbach resonance with formation of a molecular ion in the $(b_1)(b_1^*)^2\ {}^2B_1$ state (point group C_{2v}, with b_1 the orbital occupied by electrons of the lone pair on the sulphur atom, and a_1 the first vacant orbital), it becomes clear why CH_3^- ions (${}^1A_1$) are absent from peak (II), since SCH_3^- ions (ground state ${}^1A$, point group C_{3v}) and the $CH_3^{\bullet}$ radical in the ground state ${}^2A_{1g}$ do not correlate with the B_1 state of the molecular ion. Peaks (III) and (IV) of dimethyl sulphide represent S^-, SCH_3^-, CH_3^-, CH_2^-, and $(M - H)^-$ ions, and probably result from the dissociation of resonant states, of the corresponding (by Feshbach resonance) Rydberg states of the molecule. Dissociative electron capture in the other dialkyl sulphides investigated is similar to that in dimthyl sulphide, but peaks (III) and (IV) are replaced by one broad resonance peak (Fig. 2).

In contrast to aliphatic sulphides, the negative molecular ions of cyclic sulphides (thiophans) have corresponding mass spectra containing intense lines due to $(M - H)^-$ ions, the relative yield of which increases with the length of the alkyl group. With electrons of energy 8 eV decomposition occurs according to the scheme[75]



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Ions corresponding to single-particle resonance were not detected, which is fully explained by the fact that the energy available is insufficient to rupture two bonds on addition of an electron to the antibonding orbital of the sulphur–carbon bond.

Alkyl benzyl and phenyl sulphides are interesting in containing both a benzene ring and sulphur–carbon bonds, so that dissociative electron capture by their molecules can be compared with corresponding processes in benzenes and in dialkyl sulphides. Benzyl ethyl, methyl, and propyl sulphides, as well as butyl, ethyl, methyl, and propyl phenyl sulphides, have been studied[51]. With electrons of energy 0–10 eV three peaks can be distinguished, as in dialkyl sulphides. With alkyl benzyl sulphides the first peak (single-particle resonance) is characterised by a very large ion-formation cross-section ($\sigma \simeq 10^{-15}$ cm^2), and the ions SR^-, CH_3^- (in benzyl methyl sulphide), and $C_6H_5CH_2^-$ are observed in the second peak. The absence of $C_6H_5CH_2S^-$ ions indicates that the second peak is due to excitation of the lone pair of electrons on the sulphur atom. The large formation cross-section of SR^- ions in the second peak ($\sim 10^{-17}$ cm^2) is explained by formation of the benzyl radical in the ${}^2B_1$ state: $(C_6H_5CH_2SR)^{-*} \rightarrow C_6H_5CH_2^{\bullet}\ ({}^2B_1) + SR^-\ ({}^1A_1)$. The ions $(M - H)^-$, SH^-, S^-, SR^-, and $C_6H_5CH_2S^-$ are observed in the third resonance peak.

Thus the benzene ring in alkyl benzyl sulphides does not trap electrons, the overall pattern of dissociative electron capture being determined by the molecular orbitals of the sulphur–carbon bonds. The ion-formation cross-sections are larger than with dialkyl sulphides. The benzene ring has a more significant effect in alkyl phenyl sulphides, since processes characteristic of alkylbenzenes are observed (the ions C_2H^-, $C_4H_3^-$, $C_5H_5S^-$, and C_2H^- in the third peak—Fig. 6). Increase in size of the alkyl radical makes the mass spectrum more "sulphidic": thus the formation only of C_2H^- ions in the spectrum of butyl phenyl sulphide indicates the presence of the benzene ring; the other ions are formed by processes analogous to the fragmentation of dialkyl and alkyl benzyl sulphides.

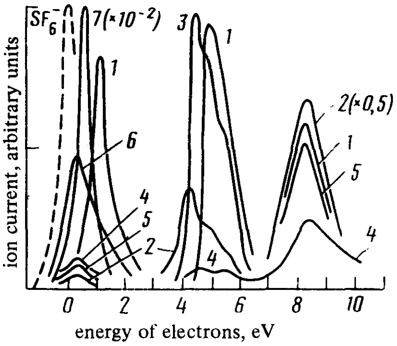


Figure 6. Effective-yield curves for negative ions from methyl phenyl sulphide: 1) S^-; 2) SCH_3^-; 3) CH_3^-; 4) $C_6H_5^-$; 5) SH^-; 6) SC_2H^-.

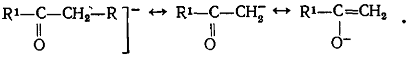
The existence in alkyl phenyl sulphides of a combined system comprising the ring π-electrons and the lone pair of electrons of the sulphur atom leads in the second peak to the appearance of complicated effective-yield curves, as would be expected. Fig. 6 shows that several closely spaced states of the molecular ion undergo decomposition, with the appearance of "bulges" and inflexions on the effective-yield curves of the ions.

9. Carbonyl Compounds

Study of the scattering of monoenergetic electrons on carbon monoxide have shown the existence of several Feshbach resonances in the range of electron energies 10–12.2 eV [76] and single-particle resonance at 1.7 eV. [77] The latter type of resonance has been observed also in acetaldehyde, acetone, acetophenone, benzophenone, and benzaldehyde (at 1.2, 1.2, 0.95, 0.75, and 0.72 eV). [78] In acetone it is not accompanied by formation of negative ions. When acetone molecules interact with electrons, negative ions appear as a broad peak resulting from the superposition of several resonance peaks over the range of electron energies 7–11 eV. [79,80]

Formation of chloride ions in chloroacetone is energetically possible by dissociation of a single-particle resonant state. The maximum yield of Cl^- ions is situated at 0.6 eV. Capture of thermal electrons by hexafluoroacetone yields negative molecular ions that are long-lived with respect to autoionisation ($\tau > 10^{-6}$ s). The introduction of fluorine atoms evidently lowers the energy of the π-orbital of the carbonyl group to such an extent that the electron affinity of the molecule becomes positive.

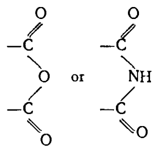
The main processes producing negative ions in aldehydes and ketones are rupture of a β-carbon–carbon bond relative to the carbonyl group and the formation of homologous ions CH⁝C.O⁻ (*m/e* 41), CH_3.C⁝C.O⁻ (55), etc:



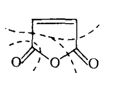
$$\left[R^1{-}\underset{\underset{O}{\parallel}}{C}{-}CH_2{-}R\right]^- \leftrightarrow R^1{-}\underset{\underset{O}{\parallel}}{C}{-}CH_2^- \leftrightarrow R^1{-}\underset{\underset{O^-}{|}}{C}{=}CH_2 \; .$$

Formation of the ions O^- and OH^- (with rearrangement of bonds), hydrocarbon ions CH_2:CH^- (*m/e* 27), and R_1–CO^- ions has also been observed[80].

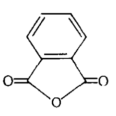
Two resonance peaks of ion emission have been found by Cooper and Compton[81] both in acetic anhydride and in acetyl peroxide. The first resonance peak represents CH_3COO^- ions (maximum yields at ~1 and at ~0 eV respectively), and the second peak CH_3^- and O^- ions (maxima at ~7 and at ~6.6 eV). These workers also investigated the capture of electrons by molecules containing the configuration



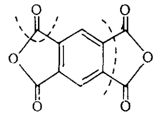
as part of a five- or six-membered ring. Unsaturated compounds



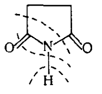
τ = 250 μs



τ = 330 μs

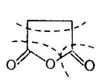


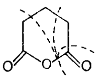
τ = 8000 μs

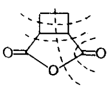


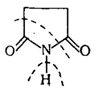
τ = 43 μs

trap thermal electrons with the formation of long-lived molecular ions (the mean lifetimes before ejection of the electron are indicated under the above structural formulae). In saturated compounds









only the formation of short-lived molecular ions is observed. The most probable process entailing dissociation negative molecular ions of the above compounds is ejection of carbon monoxide with formation of $RCOO^{-}$* ions, which are metastable with respect to detachment of an electron. Similarly metastable CO_2^{-}* ions are also observed, as well as O^-, CH_2CO^-, CO^-, and other ions corresponding to breakdown of the molecular ions in the ways indicated by the broken lines on the above structural formulae.

Dissociative electron capture by keten[82] and formaldehyde[83] has also been investigated.

10. Peroxides

The mass spectra of t-butyl and of its hydroperoxide are almost identical[84]. Over the range of electron energies 0–3 eV the ions $(CH_3)_3CO^-$, CH_2:$C(CH_3).O^-$, and CH_3^- are observed (100%, 13%, and 0.1% respectively), with a metastable-ion peak corresponding to the transition

$$(CH_3)_3CO^- \xrightarrow[\bullet]{-CH_4} CH_2{=}C(CH_3)O^- \; .$$

m/e 73 *m/e* 57

It was supposed that *m/e* 73 ions were formed by the direct capture of electrons by t-butoxy-radicals produced by thermolysis of the compounds in the ionisation chamber.

Investigation of dissociative electron capture by $R.C(CH_3)_2OOH$ molecules (where R = CH_3, C_2H_5, C_6H_5, $C_{10}H_7$) and by perbenzoic acid indicates[85,86] that the main process with all the compounds, when low-energy electrons are trapped, is the formation of $(M - OH)^-$ ions, in an autoionisation state, i.e. in an excited state with an average lifetime of $\sim 10^{-3}$ s before spontaneous ejection of an electron. The mass spectra contain a metastable-ion peak corresponding to the transition

$$R(CH_3)_2O^- \xrightarrow[\bullet]{-CH_4} RC(CH_2)O^- \; .$$

In the mass spectrum of perbenzoic acid the transitions

$$(C_6H_5CO{-}OOH)^- \xrightarrow[\bullet]{-OH} C_6H_5CO_2^- \xrightarrow[\bullet]{-CO_2} C_6H_5^-$$

are observed.

11. Nitro-compounds, Nitrites, [Nitrates,] and Nitriles

A relatively large number of papers have been published on the capture of electrons by nitromethane[65,87-90], whose negative molecular ion has six resonant states, which dissociate with the formation of negative ionic fragments[90]. Table 5 gives only ions from primary processes of electron capture, but $CH_2NO_2^-$ and $CHNO_2^-$ have also been observed, resulting from secondary reaction of O^- ions with nitromethane molecules, as well as OH^- and CH_2NO^- ions produced by an ion–molecule reaction involving NO_2^-.

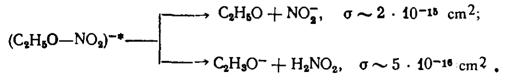
Table 5. Negative ions from nitromethane (relative intensity of NO_2^- ions at 0.6 eV taken as 10 000).

Electrons, eV	Ion	Relative intensity	Electrons, eV	Ion	Relative intensity
0.6	NO_2^-	10 000	7.8–7.9	$CH_2NO_2^-$	37.5
3.7	CH_2NO^-	5		CH_2NO^-	25
	CNO^-	10	8.3	NO^-	2.5
	CN^-	10		CNO^-	10
	OH^-	50		OH^-	37.5
	CH^-	2.5		CN^-	10
5.6	O^-	250			
	OH^-	—			

A rather lower yield of negative ions is obtained in nitroethane[65] than in nitromethane, and the maxima on the effective-yield curves are displaced to higher energies (by a few tenths of an electron-volt).

Nitrites are characterised[65,91] by a large cross-section for ion-formation (~10^{-15} cm^2) on the capture of thermal electrons, by the reaction Alk.O.N:O^- → $AlkO^-$ + NO. The effective cross-section diminishes as the alkyl chain becomes longer. Formation of NO^- and NOH^- ions also occurs.

The ·O–NO_2 bond in ethyl nitrate also readily undergoes cleavage when the molecule traps an electron of energy close to zero:



$$(C_2H_5O{-}NO_2)^{-*} \begin{cases} \longrightarrow C_2H_5O + NO_2^-, & \sigma \sim 2\cdot 10^{-15}\ \text{cm}^2; \\ \longrightarrow C_2H_3O^- + H_2NO_2, & \sigma \sim 5\cdot 10^{-16}\ \text{cm}^2 \; . \end{cases}$$

Rupture of the O–NO_2 bond is also involved in the reactions

$$(C_2H_5O{-}NO_2)^- \longrightarrow \begin{cases} C_2H_5O^- + NO_2, & \sigma \sim 6 \cdot 10^{-17}\ \mathrm{cm}^2; \\ C_2H_4O^- + HNO_2, & \sigma \sim 2 \cdot 10^{-17}\ \mathrm{cm}^2. \end{cases}$$

Effective-yield curves have been obtained for the ions CN^-, $CHCN^-$, CHN^-, and CH_3CH^- from CH_3CN^- and $C_2H_5CN^-$.[38] Resonance peaks of negative-ion emission and their relative intensities have been recorded for the interaction of electrons with azoisobutyronitrile[92] and cyanonorbornene[50].

12. Peculiarities of the Formation of Negative Ions

In conclusion we make a general comparison of the dissociative electron-capture mass spectra with the mass spectra of positive ions, noting the most significant features of resonance processes.

Dissociative electron capture by molecules is characterised by a marked dependence of the effective ion-formation cross-sections on the functional groups present in the molecule. In alkyl benzyl and phenyl sulphides, nitrates, and hydroperoxides, for example, the effective cross-sections reach 10^{-14}–10^{-15} cm^2 (vibrationally excited Feshbach resonances and shape resonances); in alkenes and alkylbenzenes the cross-sections of formation of negative ions do not exceed 10^{-19} cm^2 (electronically excited Feshbach resonances)‡. Such marked differences in total ionisation cross-sections are not observed in the mass spectrometry of positive ions.

In contrast to the formation of positive ions, when most of the fragments may be positively charged, the extra electron can be retained only by fragments whose electron affinity is positive. For example, processes involving formation of N^- ions are excluded in nitrogen-containing compounds, since the electron affinity of the nitrogen atom is negative; this is probably why $C_2H_5^-$ ions are not formed, although detachment of $C_2H_5^{\cdot}$ radicals is observed in dissociative electron capture by molecules containing alkyl chains. The small number of lines in such mass spectra in comparison with those of positive ions undoubtedly is largely due to the fact that not all possible channels of decomposition of a negative molecular ion yield fragments having positive electron affinities. However, the existence of several resonant states of molecular ions to some extent compensates for the paucity of lines in the dissociative electron-capture mass spectra. In many cases we can speak of several such mass spectra of a given substance according to the number of resonances observed.

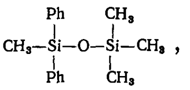
Dissociative electron capture via electronically excited Feshbach resonances usually involves a large excess energy, so that ionic fragments are likely to be formed in vibrationally excited states. Dissociation of the molecular ions thus occurs in ways leading to ionic fragments whose energy of vibrational excitation is less than some critical value, since a high energy of vibrational excitation may cause either further dissociation of the ionic fragment or ejection of the extra electron within times $\tau < 1$ μs (ions with such short lifetimes are not recorded by the mass spectrometer). Negative ions of energetically less advantageous structures are often formed preferentially precisely because of their lower energy of vibrational excitation[94]. It is noteworthy that, in the mass spectrometry of positive ions, the stability of the fragments formed plays an important role in determining the predominant direction of dissociation, where stability of the decomposition products implies mainly energetically favourable structures of the ion and of neutral fragments.

The finite lifetime of negative molecular ions before spontaneous detachment of an electron restricts the possible processes of dissociation. As a consequence, a smaller contribution is made by processes involving rearrangements, which require times comparable with that for detachment of the electron. For this reason negative ionic fragments are formed almost solely by simple cleavage of bonds in the molecular ion[86,94,95].

Table 6. Dissociative electron-capture mass spectra of isomers (I) and (II).

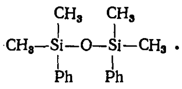
m/e	Relative intensity		*m/e*	Relative intensity		*m/e*	Relative intensity	
	I	II		I	II		I	II
285	100	8.0	211	13.0	—	135	—	2.0
269	25.0	6.0	207	60.0	100	89	32.0	5.0
213	13.0	—	151	—	7.5	73	16.0	2.4

For the above reasons the dissociative electron-capture mass spectra of structural isomers show marked differences. In contrast, the intensity of rearrangements makes the positive-ion mass spectra of structural isomers either completely identical or only slightly different (cf. e.g. the two types of mass spectra for polyenes and mass spectra of the former type for two isomeric propylthiophens—Figs. 4 and 5). Another illustration is provided[86] by the preparation of two isomers of molecular weight 286 and composition $Si_2O(CH_3)_4(C_6H_5)_2$ as shown by elementary analysis, infrared spectra, and positive-ion mass spectra. However, these mass spectra gave no indication of the isomeric structures, since they were almost identical for the two specimens. The dissociative electron-capture mass spectra (Table 6) make it easy to assign the structures



$$CH_3{-}\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{Si}}{-}O{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}{-}CH_3,$$

(I)



$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Ph}{|}}{Si}}{-}O{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Ph}{|}}{Si}}{-}CH_3.$$

(II)

The great sensitivity of dissociative electron-capture mass spectra to variation in molecular structure follows from the conditions of dissociation of the parent molecular ion. The identification of isomeric structures may therefore be a possible field for the practical application of this type of mass spectrometry.

IV. SOLUTION OF SPECIAL PROBLEMS BY NEGATIVE-ION MASS SPECTROMETRY

1. Recording of Free Radicals in the Gas Phase

Iminoxyl radicals (di-t-butyliminoxyl and 2,2,6,6,-tetramethylpiperidinoxyl), on trapping thermal electrons, form negative molecular ions with $\tau = 16$ and 21 μs respectively,

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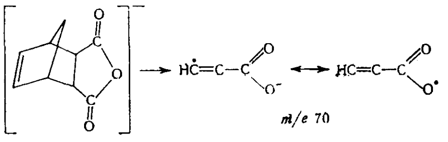
‡ Differences in the effective ion-emission cross-sections can be used to solve several problems in determining minor quantities of one substance in another[93].

the effective cross-section of the process being $\sim 10^{-17}$ cm^2.

Positive-ion mass spectrometry cannot record iminoxyl radicals, since their spectra contain no characteristic fragments, and in the presence of impurities it is impossible to isolate the spectrum corresponding to the radical[96] (the use of electron spin resonance spectra is applicable only to the liquid phase). The recording of iminoxyl radicals from the peaks of negative molecular ions is free from the problems of "background" and the superposition of peaks due to impurities, since the probability that the resonance peaks of ion emission for the radical and for the impurity molecules will coincide, with simultaneous coincidence of the mass numbers of the ions, is very slight[92, 97].

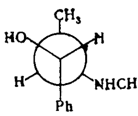
2. Stereoisomerism of Organic Compounds

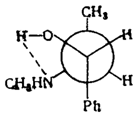
Examination of the spectra of *endo*- and *exo*-5-cyanonorbornenes and of *endo*- and *exo*-norbornenedicarboxylic acids has shown that their differences can be used to identify stereoisomeric derivatives of norbornene and related bicyclic compounds. Thus the effective yield of *m/e* 70 ions from *endo*-norbornenedicarboxylic acid reaches a maximum with electrons of energy 6 eV, whereas with the *exo*-isomer the maximum is located at 4.7 eV. This means that $(H_2C_2CO_2)^-$ ions having *m/e* 70 can be formed, with maximum yields at 6 and 4.7 eV, by two resonance processes from both molecules



but the probability ratios of these processes are different. This applies also to the formation of ions with *m/e* 52, 91, 103.[95]

Ephedrine and pseudoephedrine exist predominantly as the respective conformers[98]


(I)


(II)

.

Considerable differences in the relative intensities of peaks due to ions of the two isomers are observed only with certain mass lines[99]. Fig. 7 shows the dependence of the total currents of negative ions of (I) and (II) on the energy of the electrons. Thus the stereochemical differences do not result in the appearance of new resonant states of the molecule–electron system. However, the absolute effective capture cross-sections of electrons change in all the resonance peaks other than the second, which is due to $(M - H)^-$ ions. The cross-sections for formation of negative ions of ephedrine in the resonance peaks *1* and *3* are somewhat lower than for pseudoephedrine, but at peak *4* they are almost double. Ephedrine is characterised by an increased relative probability of formation of ions having *m/e* 146, 133, and 117, whereas in pseudoephedrine the proportion of ions having *m/e* 17 and 30 increases. The effective-yield curves for ions from the two isomers differ markedly in the region of electron energies of ~6.5 eV. Many other quite significant differences between the spectra of ephedrin and pseudoephedrine have been discussed[97]. The positive-ion mass spectra of the isomers, obtained under standard conditions, are almost identical.

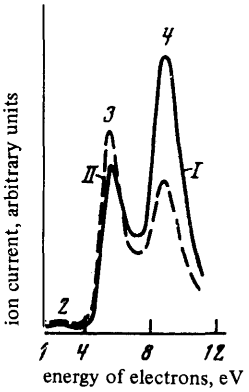
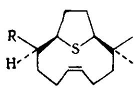
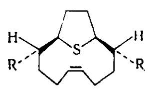


Figure 7. Dependence of total ion current on energy of electrons for: I) ephedrine; II) pseudoephedrine.

Study of the stereochemistry of 13-thiabicyclo-[8,2,1]tridec-*cis*-5-ene derivatives





has shown that, when R = H, no new states of the negative molecular ion appear in comparison with dialkylthiophans. The situation is greatly changed by the introduction of two acetoxy-groups ($R = OCOCH_3$). In particular, ions having *m/e* 119 are detected, with the empirical formula $(OCOCH_3)_2H^-$. Since peaks due to metastable and rearranged ions are absent from dissociative electron-capture mass spectra, it was concluded[100] that the negative molecular ions exist in an excited state for only a short time. From this point of view the formation of *m/e* 119 ions indicates the steric proximity of the acetoxy-groups in the thiabicycloalkane diacetate. Ions of type $(R_2H)^-$ are also detected in the spectra of thiabicycloalkanes with $R = OCH_3$, NO_2. These results have provided part of the evidence for the *cis*-arrangement of the substituents in 2,9-disubstituted derivatives of 13-thiabicyclo[8,2,1]tridec-*cis*-5-ene.

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The results given in this Review of the mass spectra of negative ions in the dissociative capture of electrons by organic molecules cover little more than a hundred individual compounds belonging to 10–15 classes, incomparably fewer than the data on the mass spectra of positive ions. It is not surprising, therefore, that there remain many unsettled questions on the mechanism of dissociation accompanying the capture of electrons by molecules. It is indisputable that further work is needed on such problems as e.g. the structure of ions and neutral fragments, the internal energy of excitation of the resulting ions, and the classification of resonant states of the molecule–electron system.

Nevertheless, the material presented here is in our opinion evidence that even now we can regard such mass spectrometry of negative ions as a method which may be useful in solving several specific problems in organic chemistry.

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Hydrogenation of Alkenes on Oxide Catalysts

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A qualitative survey of available data has enabled pure oxides to be divided into five groups according to their catalytic activity. Zeolites are less active than oxides corresponding to their cationic forms. The activity of an oxide catalyst either increases continuously or passes through a maximum with increase in its temperature of ignition. This type of dependence is explained by the surface dehydroxylation model on the assumption that the activity is determined by the presence of electron-donating and electron-accepting sites situated side by side on the surface. The hydrogenation of alkenes involves stages of activation of the alkene and of hydrogen, with on most oxides appearance of a semi-hydrogenated form. A list of 91 references is included.

CONTENTS

I. INTRODUCTION

The problem of the hydrogenation of alkenes on oxide catalysts began to attract the attention of research workers only during recent years. Oxides, though less active than metals[1-3], may in several cases have the advantages of being less sensitive to certain catalytic poisons, more highly selective, and easily regenerated. In spite of the large number of experimental investigations, hardly any reviews have appeared covering this field of catalysis. A survey[4] of the conversion of alkenes on oxides contained a short list of references up to 1960.

In the present Review the problem of the hydrogenation of alkenes on oxide catalysts is considered from the points of view of the choice of catalyst, the nature of the catalytic activity, and the kinetics and mechanism of the hydrogenation of alkenes. Factual material is given illustrating the features of reactions on various oxides and on certain multicomponent systems.

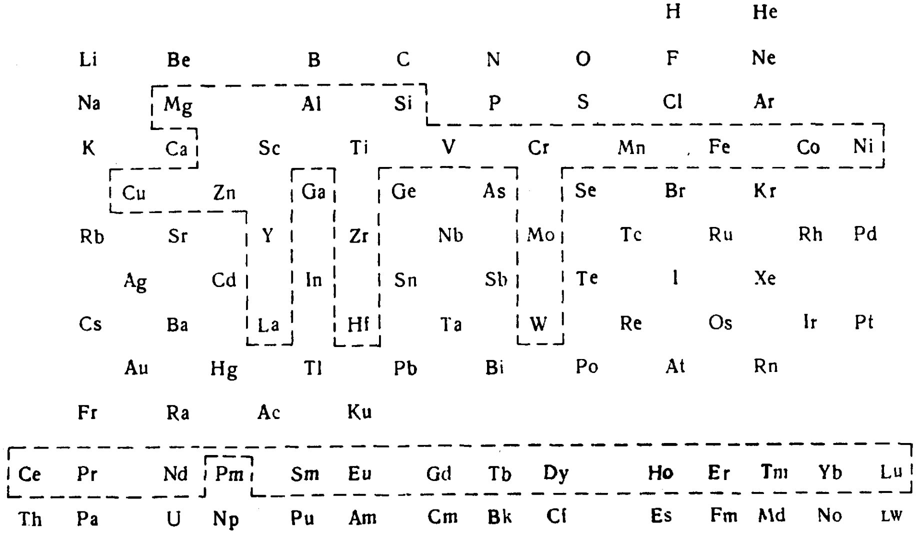
II. ACTIVITY OF OXIDE CATALYSTS

1. Individual Oxides

Thirty individual oxides (Table 1) and several mixed oxide systems have been examined as catalysts for the hydrogenation of alkenes. The largest number of investigations have been made on the oxides of zinc, aluminium, and chromium. The alkenes to be hydrogenated ranged from C_2 to C_8, most of the work being done on ethylene and propene.

Tables 2-4 give details of the conditions of preparation of the catalysts and the study of hydrogenating activity. Some 70% of the researches were made by a static method, and the remainder under flow conditions. The temperature range of the investigations was extremely wide, from −120°C for chromic oxide to 500–550°C with alumina, silica, and vanadium sesquioxide. The pressure of the

Table 1. Elements whose oxides have been investigated in the hydrogenation of alkenes.



reaction mixture under flow conditions was usually atmospheric, but in the static method it varied from 45 torrs to 60 atm. The molar ratio of hydrogen to alkene usually exceeded unity.

Table 2. Conditions of preparation and activation of oxide catalysts for the hydrogenation of alkenes.

Catalyst	Preparation and activation of catalyst	Alkene	Ref.
MgO	$MgC_2O_4 \xrightarrow[\text{air}]{450^\circ} MgO\ (400^\circ, H_2)$	C_2H_4	5
Al_2O_3	$Al(OC_3H_7)_3 \rightarrow Al(OH)_3 \xrightarrow[10^{-6}\ \text{torr}]{450-650^\circ} \gamma\text{-}Al_2O_3$	C_2H_4	6,7
	$Al(NO_3)_3 \rightarrow Al(OH)_3 \xrightarrow[\text{air}]{650-800^\circ} Al_2O_3$	C_2H_4	8
	$\beta\text{-}Al(OH)_3 \xrightarrow[\text{air}]{600^\circ} Al_2O_3\ (500^\circ, H_2)$	C_2H_4	9
	$Al(OR)_3 \rightarrow \beta\text{-}Al(OH)_3 \xrightarrow[10^{-6}\ \text{torr}]{600^\circ} Al_2O_3$	C_2H_4	10
	$Al(OC_3H_7)_3 \rightarrow Al(OH)_3 \xrightarrow[\text{vacuum}]{650^\circ} Al_2O_3$	C_2H_4	11—13
	$Al(OH)_3 \rightarrow Al_2O_3\ (500^\circ,\ \text{vacuum})$	C_2H_4	14
SiO_2	$Na_2SiO_3 \xrightarrow{HCl} H_2SiO_3 \xrightarrow{800^\circ} SiO_2$	C_2H_4	15
TiO_2	$Ti(C_2O_4)_2 \xrightarrow{NH_4OH} Ti(OH)_4 \xrightarrow[H_2]{670^\circ} TiO_2$	C_2H_4	5
	$Ti(OC_3H_7)_4 \xrightarrow{AcOH} H_2TiO_3 \xrightarrow[\text{air}]{670^\circ} TiO_2$ (anatase)	C_2H_4	16
	TiO_2 — rutile (commercial)	C_2H_4	16
V_2O_3	$(NH_4)_3VO_4 \xrightarrow[H_2]{400^\circ} V_2O_3$	C_2H_4	5
	$NH_4VO_3 \xrightarrow{HNO_3} HVO_3 \xrightarrow[H_2]{400^\circ} V_2O_3$	C_2H_4	16
Cr_2O_3	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{400^\circ} Cr_2O_3$	C_2H_4 C_3H_6 C_8H_{16}	17
	$Cr(NO_3)_3 \xrightarrow{NaOH} Cr(OH)_3 \rightarrow Cr_2O_3$	C_3H_6 C_8H_{16}	18
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[N_2]{500^\circ} Cr_2O_3$	C_2H_4 C_3H_6	19
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{450^\circ} \alpha\text{-}Cr_2O_3$	C_2H_4	16
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[\text{vacuum}]{425^\circ} Cr_2O_3$	C_2H_4	20
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{500^\circ} \alpha\text{-}Cr_2O_3$	C_2H_4	21
MnO	$MnC_2O_4 \xrightarrow[\text{air}]{450^\circ} MnO\ (400^\circ, H_2)$	C_2H_4	5
Fe_2O_3	$Fe(NO_3)_3 \xrightarrow{NH_4OH} Fe(OH)_3 \xrightarrow[O_2]{400^\circ} \alpha\text{-}Fe_2O_3$	C_2H_4	16
Co_3O_4	$Co(NO_3)_3 \xrightarrow{NH_4OH} Co(OH)_3 \xrightarrow[\text{air}]{450^\circ} Co_3O_4$	C_2H_4	16
NiO	$Ni(OH)_2 \xrightarrow[10^{-6}\ \text{torr}]{200^\circ} NiO$	C_2H_4	16
ZnO	$ZnC_2O_4 \xrightarrow[\text{air}]{450^\circ} ZnO$	C_2H_4	5
	$Zn(NO_3)_2 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[H_2]{400^\circ} ZnO\ (260^\circ,\ \text{vacuum})$	C_2H_4	16
	$ZnC_2O_4 \xrightarrow[\text{vacuum}]{450^\circ} ZnO$	C_2H_4	22
	$ZnCO_3 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[10^{-6}\ \text{torr}]{250^\circ} ZnO$	C_2H_4	23,24
	$ZnCO_3 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[10^{-6}\ \text{torr}]{400^\circ} ZnO$	C_2H_4	25,26
	$ZnO\ (300^\circ, O_2;\ 300^\circ, H_2;\ 450^\circ,\ \text{vacuum})$	C_2H_4	20
	$ZnC_2O_4 \rightarrow ZnO\ (450^\circ,\ \text{vacuum})$	C_2H_4	27
	$ZnO\ (300^\circ, H_2;\ 450^\circ,\ \text{vacuum})$	C_2H_4	28,29
	$ZnO\ (400^\circ, O_2;\ 450^\circ,\ \text{vacuum})$	C_2H_4	30
	$ZnC_2O_4 \rightarrow Zn(OH)_2 \xrightarrow{400^\circ} ZnO$	C_2H_4	31
	$ZnO\ (500^\circ,\ \text{vacuum})$	C_2H_4	32
Sc_2O_3	$Sc(OH)(NO_3)_2 \xrightarrow{NH_4OH} Sc(OH)_3 \xrightarrow[10^{-5}\ \text{torr}]{600-900^\circ} Sc_2O_3$	C_2H_4	33
Y_2O_3	$Y(NO_3)_3 \xrightarrow{NH_4OH} Y(OH)_3 \xrightarrow[10^{-5}\ \text{torr}]{600-900^\circ} Y_2O_3$	C_2H_4	33
	$Y(NO_3)_3 \xrightarrow{NH_4OH} Y(OH)_3 \xrightarrow[\text{air}]{650^\circ} Y_2O_3\ (610^\circ, H_2)$	C_2H_4 C_3H_6 C_6H_{12}	34,35
ZrO_2	$Zr(NO_3)_4 \xrightarrow{NH_4OH} Zr(OH)_4 \xrightarrow[10^{-5}\ \text{torr},\ H_2]{600-900^\circ} ZrO_2$	C_2H_4	33
Mo_2O_3	$(NH_4)_2MoO_4 \rightarrow Mo_2O_3$	C_2H_4	5
$MoO_{2\div 3}$	$(NH_4)_6Mo_7O_{24} \xrightarrow[2.\ 450^\circ\ \text{vacuum},\ H_2]{1.\ 300^\circ,\ \text{air}} MoO_{2+x}$	C_2H_4	36
Ln_2O_3	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[\text{air}]{650^\circ} Ln_2O_3\ (610^\circ, H_2)$ (Ln=La, Nd, Ho, Er)	C_3H_6	37—39
	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[10^{-5}\ \text{torr}]{600-900^\circ} Ln_2O_3$ (Ln=La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tu, Yb, Lu)	C_2H_4	33
	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[\text{vacuum}]{600^\circ} LnO_{2-x} \rightarrow$ $\xrightarrow[H_2,\ 10^{-5}\ \text{torr}]{600-900^\circ} Ln_2O_3$ (Ln = Pr, Tb, Er)	C_2H_4	33
$CeO_{2-\delta}$	$Ce(NO_3)_3 \xrightarrow{NH_4OH} Ce(OH)_3 \xrightarrow[H_2,\ \text{vacuum}]{600-900^\circ} CeO_{2-\delta}$	C_2H_4	33
HfO_2	$Hf(NO_3)_4 \xrightarrow{NH_4OH} Hf(OH)_4 \xrightarrow[10^{-6}\ \text{torr}]{600-900^\circ} HfO_2$	C_2H_4	33
WO_3	WO_3 — commercial (250°, He)	C_2H_4	40

It is evident from Tables 2-4 that quantitative comparison of oxides with respect to catalytic activity is difficult. Besides differences in methods of estimating activity, the oxides differed considerably in mode of preparation and conditions of activation. At the same time a cautious approach is necessary to assessing results obtained in individual investigations. Thus mutually different results were obtained in studies of the catalytic activity of aluminium oxide by six groups of workers[6-14,44]. Analogous differences are observed when a comparison is made of researches on the catalytic activity of the oxides of zinc[5,16,20,22-32] and vanadium[5,16,41]. Germain[45] remarks correctly that "the pretreatment of oxides is so important that some doubt must be cast on the significance of laws of hydrogenation". Another important factor determining the observed catalytic activity is the purity of the initial alkenes and hydrogen. The poisoning effect of water on the activity of oxides has now been proved. Nevertheless, the degree of purification of the gases was not indicated in the papers cited above. Thus the data in Tables 3 and 4 permit only certain qualitative conclusions on catalytic activities.

Table 3. Activity data on oxide catalysts for the hydrogenation of alkenes, obtained by the static method.

Oxide	Alkene	Reaction conditions			Activity* mole m^2 s^{-1} (temp., °C)	Ref.
		temp., °C	pressure of mixture, torrs	$\frac{H_2}{C_nH_{2n}}$		
MgO	C_2H_4	400	760	1.6	0	5
Al_2O_3	C_2H_4	350—450	500	1.0	($\tau_{0.5}$ = 12 min) (450°)	6,7
	C_2H_4	100—200	600	1.0	0	14
SiO_2	C_2H_4	350—500	50—100	1	$6\cdot10^{-11}$ (350°)	15
TiO_2	C_2H_4	400	760	1.2	0	5
	C_2H_4	400	45	2	$1.4\cdot10^{-11}$	16
V_2O_3	C_2H_4	400	760	1	0	5
	C_2H_4	400	45	2	$1,2\cdot10^{-9}$	16
	C_2H_4	400—550	300—600	0.5—2	$1.3\cdot10^{-8}$ (500°)	41
Cr_2O_3	C_2H_4, C_3H_6, C_8H_{16}	350—370	760	1	—	17
	C_2H_4	—120	45	2	$6.3\cdot10^{-8}$	16
	C_2H_4	—78	300	2	—	20
	C_2H_4	0÷40	—	—	—	21
MnO	C_2H_4	400	760	1.5	0	5
	C_2H_4	400	45	2	0	16
Fe_2O_3	C_2H_4	140	75	2	$0.3\cdot10^{-10}$	16
Co_3O_4	C_2H_4	20	45	2	$1.5\cdot10^{-8}$	16
	C_2H_4	—78—30	20—70	1	—	42
NiO	C_2H_4	100	45	2	$2\cdot10^{-9}$	16
	C_2H_4	140	60 (atm)	0.5	—	43
CuO	C_2H_4	180	60 (atm)	0.5	—	43
ZnO	C_2H_4	400	760	1.2	($\tau_{0,05}$ = 60 min)	5
	C_2H_4	100	45	2	$0.9\cdot10^{-8}$	16
	C_2H_4	39—218	600	1.5	$2\cdot10^{-10}$ (56°)	22
	C_2H_4	140—162	50—200	0.5—2	$4\cdot10^{-14}$ (25°)	23, 24
	C_2H_4	80—400	30—300	1	—	25, 26
	C_2H_4	25	300	2	—	20
	C_2H_4	25—60	150	10	$5.5\cdot10^{-9}$ (25°)	27
	C_2H_4	20	130	10	—	28
	C_2H_4	20	130—400	3—10	$5\cdot10^{-9}$	29
	C_2H_4	105—120	100	1	—	31
	C_2H_4	0—30	300	2	—	32
Mo_2O_3	C_2H_4	400	760	1.5	($\tau_{0.01}$ = 60 min)	5
MoO_x	C_2H_4	250	200—700	3	0	36
Sc_2O_3	C_2H_4	—78—20	10	1.2	$0.16\cdot10^{-9}$ (—78°)	33
Y_2O_3	C_2H_4	—78—20	10	1.2	0.6 10^{-9}(—78°)	33
ZrO_2	C_2H_4	20—400	10	1.2	0	33
Ln_2O_3**	C_2H_4	—78—20	10	1.2	$3.4—0.1\cdot10^{-9}$ (—78°)	33
HfO_2	C_2H_4	—55	10	1.2	$0.06\cdot10^{-9}$	33

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* In several cases the activity is expressed as the time τ required to reach a specified degree of conversion.

** Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu.

From the above results it may be supposed that the oxides of titanium, iron, silicon, molybdenum, magnesium, and manganese are almost inactive, while those of aluminium, vanadium, and nickel exhibit slight activity. Cobalt and zinc oxides are moderately active. The most active are chromic oxide, rare-earth metal oxides, and the analogous yttria and scandia, which approach metals in their catalytic properties. Thus chromium and lanthanum sesquioxides are able to catalyse the hydrogenation of ethylene even at -120°C.[33]

A semiquantitative comparison is possible for three groups of oxides. Thus Lazier and Vaughen[5] used a recirculation method to compare the activities of magnesium, titanium(IV), vanadium(III), chromium(III), manganese(II), zinc, and molybdenum(III) oxides. The catalysts differed in method of preparation, but the conditions of activation—treatment with hydrogen at 400°C—were the same (Table 2). Chromic oxide was more active than the zinc and molybdenum oxides; the remaining oxides were inactive. On the whole these results agree with subsequent investigations. Other workers[16] have also found manganese(II) oxide to be inactive. However, varying the conditions of preparation and pretreatment has revealed some slight activity in titanium and vanadium oxides[16,41].

Table 4. Activity data on oxide catalysts for the hydrogenation of alkenes, obtained by the flow method.

Oxide	Alkene	Reaction conditions				Conversion, % (reaction rate, mole m^2 s^{-1}, at, °C)	Ref.
		temp., °C	pressure of mixture*, abs. atm	$\frac{H_2}{C_nH_{2n}}$	space velocity, h^{-1}		
Al_2O_3	C_2H_4	500	1	5	650	79	8
Al_2O_3	C_2H_4	120—430	0.25	6.5	60 000	(10^{-9}, 200°)	9
Al_2O_3	C_2H_4	200	0.3	8.7	60 000	($1.4\cdot10^{-9}$)	10
Al_2O_3	C_2H_4	—20—240	0.01—0.2	—	—	—	11—13
Cr_2O_3	C_3H_6	200	1	3	200	98	18
	C_8H_{16}	350	—	34	3 400	79	18
ZnO	C_2H_4	0	0.001—0.07	—	60 000	—	30
Y_2O_3	C_2H_4	110	0.5	5	576	100	34, 35
	C_3H_6	185	0.5	3	192	76	34, 35
	C_6H_{12}	320	0.5	—	216	75	34, 35
La_2O_3	C_3H_6	140—210	0.5	3	600—3 000	23—40	37—39
Nd_2O_3	C_3H_6	140—210	0.5	3	600—3 000	49—81	37—39
Ho_2O_3	C_3H_6	140—210	0.5	3	600—3 000	43—72	37—39
Er_2O_3	C_3H_6	140—210	0.5	3	600—3 000	35—59	37—39
WO_3	C_2H_4	125—250	1	5	1 000	($1.6\cdot10^{-7}$, 25°)	40

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* Total pressure brought to 1 abs. atm with nitrogen or helium.

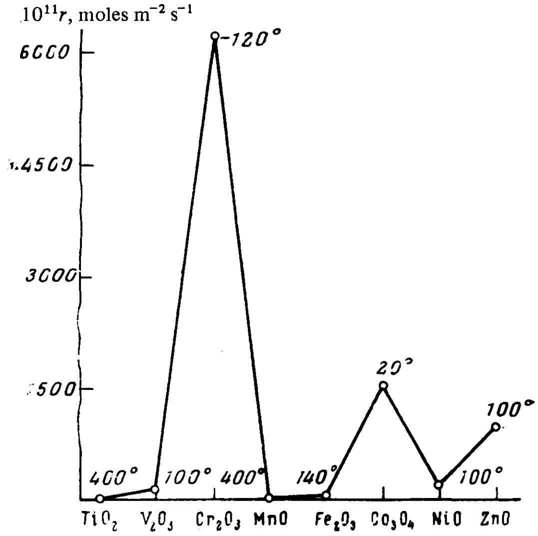


Figure 1. Catalytic activity of oxides of elements in the first transition series towards the hydrogenation of ethylene at various temperatures, where r is the reaction velocity.

Harrison et al.[16] examined the catalytic activity of oxides of transition elements in the fourth period (with the exception of scandium and copper oxides) towards the hydrogenation of ethylene. Comparison of the oxides was not altogether rigorous, for methods of preparation and conditions of activation varied considerably. Furthermore, initial rates of hydrogenation on these oxides were determined at different experimental temperatures. The two-peak pattern of catalytic activity obtained for this series of oxides (Fig. 1) was explained in terms of the electron configuration of the cations containing 3*d* electrons, in conformity with Dowden's ideas[46]. Increase in the coordination number of the cations Cr^{3+} and Co^{3+} from 5 to 6, in contrast to other cations, was accompanied by a greater gain in stabilisation energy of the crystal field. Hence adsorption or other stage accompanied by a change in coordination number was assumed to be the limiting stage. The two-peak pattern of variation in catalytic activity in the series of transition-metal oxides in the fourth period has been confirmed[47] in a study of the hydrogenation of propene by a pulse microcatalytic method.

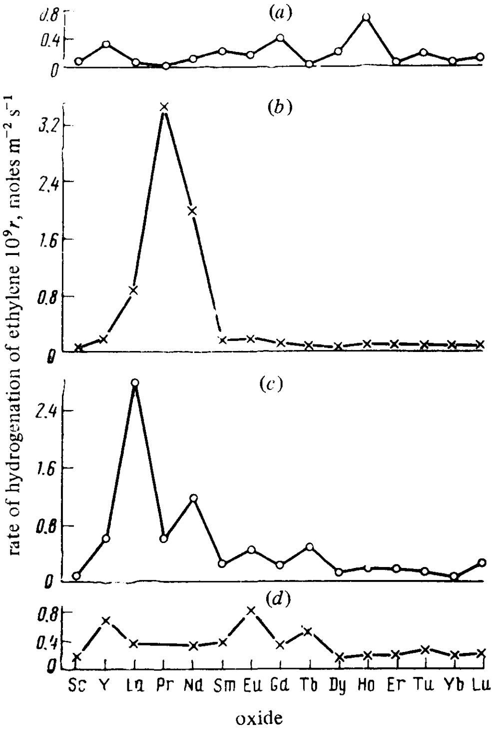


Figure 2. Catalytic activity of rare-earth sesquioxides at different temperatures (after ignition at different temperatures, °C): *a*) 20 (600); *b*) −78 (700); *c*) −78 (800); *d*) −78 (900).

An investigation has been made[33] of the catalytic activity of oxides of rare-earth metals from lanthanum to lutetium, as well as the oxides of scandium, yttrium, zirconium, hafnium, and chromium, towards the hydrogenation of ethylene. All the catalysts were prepared in the same way and were conditioned in a vacuum (to 10^{-5} torr) at various temperatures. Praseodymium, cerium, and terbium oxides were also hydrogenated and the reduced specimens were further conditioned in a vacuum at the same temperature.

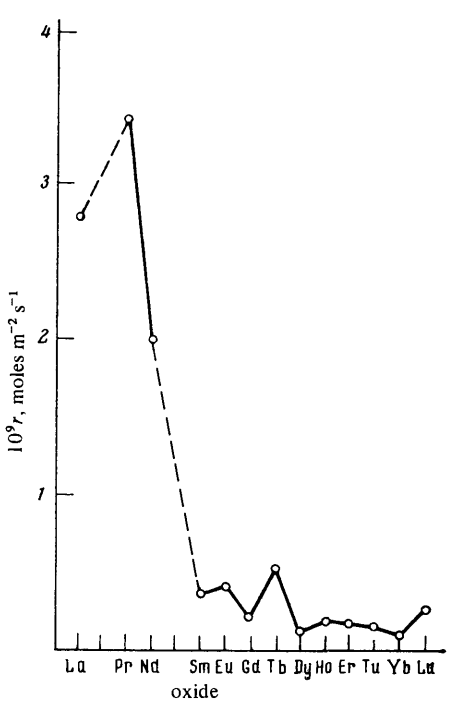


Figure 3. "Maximum" catalytic activity of rare-earth sesquioxides in the hydrogenation of ethylene at −78°C.

The catalytic activity of lanthanum, praseodymium, and neodymium oxides passed through a maximum with increase in the temperature of ignition; with all the other rare-earth sesquioxides the activity increased steadily. This feature of the behaviour of the three oxides was due to their ability to undergo a polymorphic transformation over the temperature range 600–900°C, from a body-centred cubic structure (*C*-form) to a hexagonal structure (*A*-form). It was therefore assumed that the accompanying increase in coordination number of the cation (from 6 to 7) diminished the catalytic activity. A similar conclusion follows also from results for non-stoichiometric oxides of cerium, terbium, and praseodymium. The dioxides of these metals have a fluorite structure with coordination number 8, and do not exhibit catalytic activity. The appearance of activity in the terbium and praseodymium oxides after ignition at 800°C is due to their partial decomposition, leading to a structure, derived from fluorite, with a certain number of vacancies in the oxygen sublattice and some cations having coordination number < 8.

Fig. 2 shows that the law of variation of specific catalytic activity in the series of rare-earth oxides is determined by the temperature of ignition. Thus the activity of lanthanum oxide is least after vacuum treatment at 600°C, and greatest after such treatment at 800°C.

Praseodymium and neodymium oxides exhibit maximum activity after ignition at 700°C, but many other oxides at 900°C. Thus these oxides require different ignition temperatures before they develop their maximum catalytic activity. The results indicate the difficulty of comparing the catalytic activities of oxide systems.

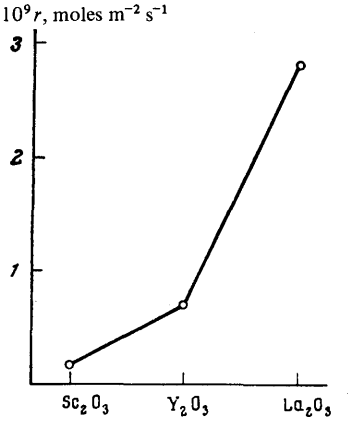


Figure 4. Activity of oxides of the scandium subgroup in the hydrogenation of ethylene at −78°C.

It has been suggested[33] that oxides should be compared after they have been ignited at temperatures ensuring maximum activity. Fig. 3 shows that such comparison gives for rare-earth oxides activities differing by factors of $10-10^2$. In this respect the rare-earth oxides differ significantly from those of transition elements in the fourth period, whose catalytic activities vary by factors of 10^2-10^3. The greatest variation in activity is observed in the series of oxides from lanthanum to gadolinium (cerium subgroup); the remaining oxides (yttrium subgroup) show a less marked variation. It is interesting that the fundamental chemical properties also show greater variation in the former than in the latter subgroup. Scandium and yttrium oxides were closely similar in catalytic activity (Fig. 4), as in many other chemical properties, to oxides of the yttrium subgroup.

Table 5. Hydrogenating activity of oxides (rate of hydrogenation of ethylene at −78°C) and electron configuration of cations.

Oxide	Configuration	$10^9 r$, mole m^{-2} s^{-1}	Oxide	Configuration	$10^9 r$, mole m^{-2} s^{-1}
Sc_2O_3	$3d^0$	0.16	La_2O_3	$4f^05d^0$	2.8
TiO_2		0.0 (Refs.5, 16)	CeO_2		0.0
Y_2O_3	$4d^0$	0.6	Lu_2O_3	$4f^{14}5d^0$	0.25
ZrO_2		0.0	HfO_2		0.01

Comparison of the activities of a few pairs of oxides (Table 5) indicates that catalytic activity does not depend solely on the electron configuration of the cation. Theoretical views suggested[46] that the activity of scandium oxide would be low, which is inconsistent with recent results[33].

The fall in catalytic activity of the oxides observed from lanthanum to lutetium and from lanthanum to scandium (Figs. 3 and 4) correlates with the decrease in their basicity[48]. This correlation explains also certain other experimental results: (i) acidic oxides—the dioxides of cerium, praseodymium, terbium, zirconium, and titanium—are not active catalysts for the hydrogenation of ethylene; and (ii) acidic impurities—oxides of nitrogen, carbon dioxide, and water—are catalytic poisons.

2. Multicomponent Oxide Catalysts

Study of a chromium–alumina catalyst in the hydrogenation of butene revealed[49] that it was relatively unstable and highly sensitive to traces of moisture, oxygen, and the treatment conditions. The butene was 5–50% hydrogenated over the temperature range 220–340°C. Hydrogenation of ethylene on this type of catalyst[50] gives yields of ethane reaching 80–90% with an equimolecular mixture of ethylene and hydrogen having a space velocity of 1000 h^{-1} at 400–470°C. The hydrogenation of propene on a potassium–chromium–alumina catalyst has been studied[51] by a pulse method at 450–600°C.

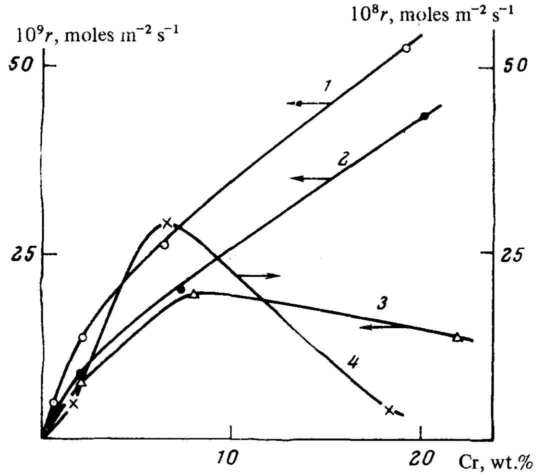


Figure 5. Rate of hydrogenation of ethylene at −78°C on alumina–chrome catalysts obtained by the impregnation with chromium trioxide of: 1) boehmite; 2) bayerite; 3) γ-alumina; 4) hydrargillite.

A circulatory static method, with an equimolecular mixture of hydrogen and ethylene at an initial pressure of 60 torrs, has been used[52] to investigate the effect of method of preparation on the activity of these types of catalyst in the hydrogenation of ethylene at −78°C. The catalysts can be divided into two groups according to the dependence of the activity on the chromium content (Fig. 5). One group includes chromium–alumina catalysts based on boehmite and bayerite (curves *1* and *2*); catalysts prepared from hydrargillite and from γ-alumina belong to the second group. Catalysts of the first group become more active with increase in the chromium content, whereas the activity of the others passes through a maximum at 7–10 wt.% of chromium.

The difference observed between the two types of chromium–alumina catalysts was explained by differences in the distribution of chromic oxide on the carrier surfaces. This involved the postulate that, with boehmite and bayerite catalysts, the proportion of Cr^{3+} ions in the surface layer increased continuously with the concentration of chromic oxide. With catalysts based on hydrargillite and γ-alumina a similar relation is observed only at low concentrations of chromic oxide. With further increase the fine crystals (or clusters) of the oxide become larger, which may lead to a decrease in the surface concentration of Cr^{3+}, and hence in catalytic activity. Catalysts based on hydrargillite are the most active: with 6–8% of chromium their activity is about tenfold that of any other chromium–alumina catalyst, and they are only slightlv inferior to chromic oxide, for which the reaction velocity under the same conditions is 50×10^{-8} mole m^{-2} s^{-1}. The introduction of potassium into a boehmite chromium–alumina catalyst diminishes the activity (Table 6).

Table 6.

Potassium, wt.%	0	0.5	1.0	2.0	4.0
$10^9 r$, moles m^{-2} s^{-1}	27	25	23	19	17

Fig. 6 illustrates the degree of conversion of ethylene into ethane on a chromium–alumina catalyst as functions of the partial pressures of water, pyridine, ammonia, and thiophenol. The toxicity of these substances towards catalysts varies in the same sequence as their acidity, which reveals the basic nature of the active centres.

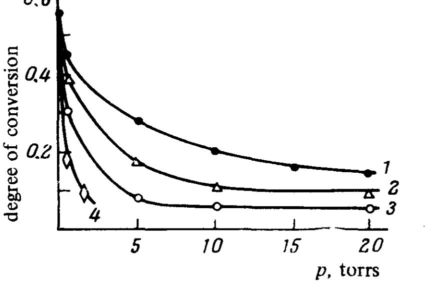


Figure 6. Kinetic isotherms for the poisoning of an alumina–chrome catalyst in the hydrogenation of ethylene at 420°C by: 1) ammonia; 2) pyridine; 3) water; 4) thiophenol.

In the presence of a zinc chromite catalyst[22] ethylene was hydrogenated at 215–250°C. On an $MoO_3.Al_2O_3$ catalyst[53], after activation with hydrogen at 500°C, ethylene was hydrogenated over roughly the same temperature range as on chromic oxide catalysts. A vanadium–aluminium catalyst is active[41] in this hydrogenation at 400–450°C. Komarevsky et al.[54–56] found that this catalyst, reduced with hydrogen at 400°C, catalysed the hydrogenation of butene, hexene, octene, butadiene, and acetylene; under 115 atm at 475°C even benzene could be 27% hydrogenated.

The hydrogenation of heptenes is strongly catalysed by $CoO.MoO_3.Al_2O_3$ over the range 250–275°C.[57] Parravano et al.[58] reported that ethylene can be hydrogenated on an aluminosilicate at 345°C, a result qualitatively confirmed by Topchieva et al.[59] According to these workers aluminosilicates catalyse the hydrogenation of propene only after pretreatment with hydrogen at 550°C. An aluminosilicate containing 0.01% of sodium was more active than a specimen containing a larger quantity. The rate of hydrogenation of ethylene diminishes with increasing acidity of aluminosilicate catalysts[60].

Table 7. Activity (measured by rate of hydrogenation) of neodymium compounds.

Compound	$10^3 r$, mol. s^{-1} Nd^{3+} ion^{-1}
Nd_2O_3, *A*-form	0.15
Nd_2O_3, *C*-form	1.2
74 mole % Nd_2O_3-CeO_2	1.2
37 mole % Nd_2O_3-CeO_2	0
$7Nd_2O_3.9SiO_2$	0.022

Several neodymium compounds have been compared with the *A*- and *C*-forms of the oxide in the hydrogenation of ethylene at −78°C (Table 7).[61] Analysis of the results revealed a relation between the activity and the coordination number of neodymium. The *C*-form of the oxide and a solid solution of 74 mole % of the oxide with cerium dioxide, containing Nd^{3+} in octahedral coordination, had similar activities per cation. The corresponding 37 mole % solid solution was catalytically inactive and contained cations only with coordination number 8. The orthosilicate $7Nd_2O_3.9SiO_2$ contained two types of cations, the relative proportions of which with 7 and 9 coordination were 2 : 5. If it is postulated that the latter cations are inactive, recalculation for cations of coordination number 7 yields a value (8×10^{-5} mol. s^{-1} ion^{-1} Nd^{3+}) very close to the activity of the *A*-form of neodymium sesquioxide with Nd^{3+} ions in the same coordination.

3. Zeolite Catalysts

Until recently few studies had been made of the influence of zeolites on hydrogenations. The activity of γ-type zeolites in the hydrogenation of ethylene was first established by Minachev et al.[62] for the neodymium, calcium, and decationised forms. Hydrogenation took place with a space velocity of 2000 h^{-1} at 78–150°C. With the conditions adopted for regeneration (treatment with air at 500°C for 2 h) the activity of the catalysts diminished from experiment to experiment. The zeolite containing neodymium was more active than the calcium and decationised forms; the sodium form was inactive. It is significant that the hydrogenation of ethylene in the presence of neodymium γ-zeolite was promoted by oxygen, which was later found to activate the hydrogenation of ethylene also with alumina[63].

Results obtained by Topchieva et al.[59,64] using a pulse method indicated that sodium, yttrium, and chromium-zeolites were active in the hydrogenation of propene at

200°C. The activity of the yttrium form depends on the temperature of pretreatment with hydrogen (200–640°C), reaching a maximum after activation at 350°C. Exchange of sodium for yttrium exceeding 50% produces sharply diminished selectivity of hydrogenation. Thus, whereas propane was the only product with yttrium γ-zeolite at a degree of exchange of 46%, the selectivity of the reaction with a specimen having 77% exchange did not exceed 30%. Similar results were obtained with the chromium form (degrees of exchange 4% and 11%). At 200°C the degree of hydrogenation on chromium γ-zeolite reached 23–50%. All specimens rapidly lost their activity. The initial activity of the sodium form was lower than those of the yttrium and chromium forms.

Table 8. Catalytic activity of zeolites and oxides in the hydrogenation of ethylene.

Catalyst	Temperature, °C		Reaction velocity, 10^3r, mol. s^{-1} ion^{-1}
	activation	hydrogenation	
0.8CrNaY; Si/Al=2.1	500	—30	3.0
	600	—30	3.1
	700	20	0.5
0.65CrNaY; Si/Al=2.5	450	—40	0.04
	500	—40	0.1
0.27CrNaY; Si/Al=2.5	500	—60	3.4
	600	—60	0.8
0.27FeNaY; Si/Al=2.5	400	400	0.1
	500	400	0.2
0.57LaNaY; Si/Al=2.1	500	20	0.2
0.22NdNaY	500	20	0.8
Cr_2O_3	500	—78	6.6
Nd_2O_3	700	—78	2.0
La_2O_3	800	—78	4.0

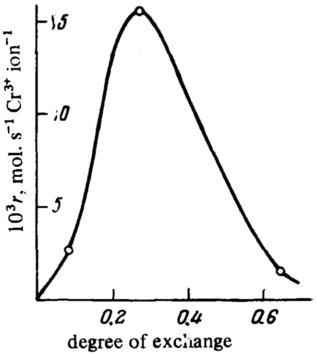


Figure 7. Dependence of activity of CrNa Y-zeolite in the hydrogenation of ethylene at 20°C on the degree of exchange of Na^+ for Cr^{3+}.

A detailed comparative investigation of the catalytic properties of various cation-exchange forms of γ-type zeolites in the hydrogenation of ethylene as functions of the type of cation, degree of exchange, and ratio of silicon to aluminium has been made[65,66] by a circulatory static method with an equimolecular mixture of hydrogen and ethylene at an initial pressure of 60 torrs. This has shown that, after vacuum treatment (10^{-5} torr) over the range 400–700°C (in steps of 100 deg), the sodium, copper, barium, calcium, and decationised forms of the zeolites were inactive from –78 to 400°C. Only zeolites containing tervalent cations—chromium, lanthanum, neodymium, and iron—were active (Table 8). With increase in the fraction of chromium exchange cations from 0.08 to 0.65 the catalytic activity passes through a maximum at a degree of exchange of 0.27 (Fig. 7).

Increasing the ratio of silicon to aluminium from 2.1 to 2.5 (cf. 0.8 CrNa and 0.65 CrNa Y-zeolites [Table 8]) leads to a change in catalytic activity. These results suggest non-uniformity of the active centres, probably due to differences in the distribution of cations among several possible sites[67]. Table 8 indicates also that the chromium form of the zeolite acquires its maximum activity after being heated in a vacuum at 500°C, which was the optimum temperature also for other cationic forms. Ignition at temperatures above 600°C caused irreversible loss of activity, although the zeolites retained their crystalline structure. This peculiarity of behaviour can be attributed to migration[67,68] of cations from large to small cavities, so that ion-exchange cations may form part of the active centres of hydrogenation. This hypothesis is supported by the qualitative analogy between the catalytic properties of oxides and zeolites. Oxides of tervalent elements form the activity sequence

$$Cr_2O_3 > La_2O_3 > Nd_2O_3 \gg Fe_2O_3,$$

which on the whole is consistent with that of the zeolites

$$\mathrm{CrNaU} > \mathrm{NdNaU} > \mathrm{LaNaU} \gg \mathrm{FeNaU}.$$

The activation energies for the hydrogenation of ethylene on oxides and zeolites are roughly equal at 3–6 kcal mole^{-1}. The lower activity of zeolites than of oxides may evidently be attributed to steric inaccessibility of some of the ion-exchange cations.

Table 9.

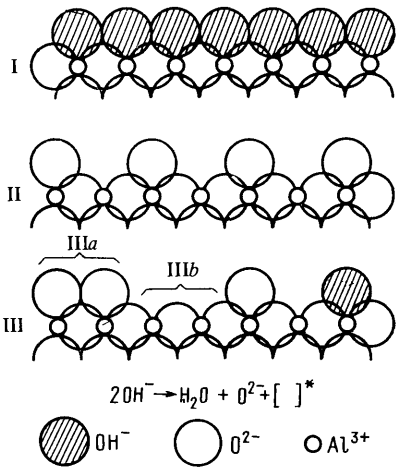
Zeolite	NaM	LiM	KM	CaM	MgM	ZnM	CdM	HM
Cyclohexane, %	98.3	87.7	11.0	98.6	69.4	59.7	17.4	19.7

Cationic forms of mordenite were first shown by Minachev et al.[69-71] to catalyse the hydrogenation of ethylene and benzene. Under the conditions adopted—$4H_2 + C_2H_4$ with space velocity 750 h^{-1} under 1–30 atm at 215–235°C—ethylene was completely hydrogenated in the presence of NaM zeolite; with the potassium form hydrogenation was 20–92% complete. Table 9 gives the yields of cyclohexane from the hydrogenation of benzene (C_6H_6 + $5H_2$ at 1 h^{-1} under 30 atm at 250°C).

III. NATURE OF THE CATALYTIC ACTIVITY

Despite the differences in approach by different authors and the use of an extremely wide range of methods, only a limited number of hypotheses have been made on the nature of the catalytic activity: (i) many workers suppose that coordinatively unsaturated cations are present in the active centre; (ii) in several papers catalytic activity was associated with ions of metals in a certain valency state; and (iii) several investigators assume that an active centre contains not only cations but also oxygen ions.

The first hypothesis provided an explanation for the many experimental data on the influence of heat-treatment conditions and the reversible poisoning effect of water vapour on the catalytic activity of oxides of aluminium[6,7], zinc[24,25,28,29], chromium[16-20], rare-earth metals[33-35], and silicon[15], as well as that of zeolites[66]. On this hypothesis the reason why oxides must be ignited for catalytic activity to develop is that, under the usual conditions of storage, the surface becomes hydrated by contact with atmospheric moisture, and contains no coordinatively unsaturated ions. The increase in activity as the temperature of ignition of the oxides is raised is attributed to increase in the number of such cations. The activity of zeolites passes through a maximum as this temperature is raised, which could be explained[66] by two factors: the activity of the zeolites is increased by the appearance of coordinatively unsaturated cations at high temperatures; on the other hand, the number of cations accessible to reactant molecules diminishes because of their migration into small cavities. Incorporation of cations into active centres follows also from the identity of the activity sequences of oxides and corresponding cationic forms of zeolites.



* Anionic vacancy on surface.

Figure 8. Diagram of cross-section through surface of aluminium oxide at various stages of dehydroxylation, with the surface: I) completely hydrated; II) completely dehydroxylated; III) partly dehydroxylated.

However, no quantitative comparison between the number of cations in a certain coordination environment and catalytic activity was made in the above studies. Such comparison is now possible for alumina, whose ability to catalyse the hydrogenation of ethylene at 250–450°C appears only after heat-treatment at 450°C,[6,7] when at least 30% of the surface aluminium ions change their coordination from 6 to 5.[72] Yet according to Weller and Hindin[7] the number of active centres does not exceed 1–2% of the total number of surface ions, since at this particular coverage with water the catalytic activity of alumina is completely lost. Raising the temperature of ignition from 450 to 550°C increases the number of coordinatively unsaturated cations only by 30%, while the catalytic activity increases by a factor of 20! Thus no direct functional dependence is present between the total number of coordinatively unsaturated cations and catalytic activity.

This conclusion suggests the non-uniformity of such cations, which is clearly illustrated by Peri's model of dehydroxylated aluminium oxide[72]. The partly dehydroxylated surface (Fig. 8) contains a disordered layer of ions: at some sites (III*a*) oxygen ions accumulate in direct contact, and at others (III*b*) coordinatively unsaturated cations are situated side by side. Catalytic activity towards hydrogenation could then probably be related to sites of the latter type. Their ability to catalyse migration of the double bond in butenes had earlier been proved by Peri[73]. The number of such sites (Fig. 8—II and III) and hence also the catalytic activity of the oxide should pass through maxima with increase in the degree of dehydroxylation (and in the ignition temperature). This conclusion is consistent with results for chromic oxide[33] and zinc oxide[23].

The relation between catalytic activity and the valency state of the cations has been discussed. Chromic oxide, CrNa Y-zeolite, and chromium–alumina catalysts strongly catalysed the hydrogenation of ethylene in the absence of Cr^{2+} ions[74]. Catalysts containing a considerable quantity of Cr^{5+} and Cr^{6+} ions were inactive, which allows us to reveal the catalytic activity of Cr^{3+} ions. With cerium, praseodymium, and terbium the sesquioxides also possessed catalytic activity, but the dioxides were almost inactive. Under the experimental conditions[74] ions of bivalent rare-earth metals were not formed, and hence the activity of these elements was due to the tervalent cation.

It was postulated in most of the above papers that ethylene underwent hydrogenation on a centre containing not only a cation but also an oxygen ion, but no evidence was given. Such evidence includes[33] the relation found between catalytic activity and basicity, which may be governed[75] by the oxygen ions.

IV. KINETICS AND MECHANISM OF THE HYDROGENATION OF ALKENES

The mechanism of the hydrogenation of alkenes (mainly ethylene) has been studied most thoroughly on the oxides of aluminium, zinc, chromium, and rare-earth metals. Kinetics, infrared spectroscopy, thermal desorption, and other methods enabling the reactivity of adsorbed species to be estimated have been used. In a few cases a tracer technique was applied. Since a kinetic method has been used most frequently, we begin with an account of the principal results obtained in studies of the kinetics of hydrogenation.

Table 10 shows that many kinetic equations have been suggested. One example indicated that the reaction velocity is almost independent of the partial pressures of the components[22]. According to others[23-26,35,38,39,77] the rate is determined solely by the pressure of hydrogen or ethylene. Two formulae[41,39] were of the first order with respect to the initial reactants, and in three cases[9,48,53] equations of the type $r = kP_{H_2}P_{C_nH_{2n}}^{0.5}$ were found. Thus inspection of Table 10 indicates that the kinetic orders with respect to hydrogen and the alkene usually vary from first to zero. The rate of the reaction is unaffected by the pressure of alkanes, except in experiments with silica and $CoO.MoO_3.Al_2O_3$ catalysts. The form of the kinetic equation depends on the chemical composition of the specimen, the conditions of pretreatment, and the temperature range of the investigation (cf. *2* and *3*, *9–11*, *13* and *14* in Table 10). The activation energy of the reaction varies over a wide range, from 0 to 24 kcal mole^{-1}, probably being a function of temperature. With the oxides of aluminium, zinc, and rare-earth metals the activation energy falls to zero with rise in temperature.

Table 10. Kinetic equations and activation energies of hydrogenation of alkenes on oxides.

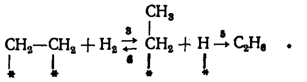
No.	Catalyst	Equation	Activation energy, kcal mole^{-1}	Temp. range, °C	Ref.
1	Al_2O_3	$r = kP_{H_2}P^{0,5}_{C_2H_4}$	9 0	120—180 300—430	9
2	Al_2O_3	$r = kP_{H_2}(1-\theta_{C_2H_4})\,\theta_{C_2H_4}$	7.7	—20÷25	11 *
3	Al_2O_3	$r = kP_{H_2}\,\theta_{C_2H_4}$	0	90—240	11
4	SiO_2	$r = kP_{H_2}/(1+K'P_{C_2H_4})$	8	350—500	15
5	V_2O_3	$r = kP_{H_2}P_{C_2H_4}$	22.0	400—550	41
6	Cr_2O_3	$r = kP^{1,5}_{H_2}P^{1,5}_{C_3H_6}$	18	200—350	18
7	ZnO	$r = kP^{0,1}_{C_2H_4}$	18	39—56	22
8	ZnO	$r = kP_{H_2}$	22	140—162	23, 24
9	ZnO	$r = kP_{H_2}$	22	80—125	25, 26
10	ZnO	$r = kP^{0,3}_{H_2}P^{0,7}_{C_2H_4}$	4.5	140—175	25, 26
11	ZnO	$r = kP_{C_2H_4}$	0	210—225	25, 26
12	ZnO	$r = kP^{0,5}_{H_2}\cdot\theta_{C_2H_4}$	—	20	29 *, 76
13	M_2O_3 (Y, La, Ho, Er)	$r = kP^{0,5}_{H_2}$	5—6	130—180	35, 38, 39
14	M_2O_3 (Y, La, Ho, Er)	$r = kP_{H_2}P_{C_3H_6}$	0	230—260	35, 38, 39
15	WO_3	$r = kP_{H_2}P^{0-1}_{C_2H_4}$	—	125—250	40
16	$V_2O_3\cdot Al_2O_3$	$r = k\,[a+(K_pH_2)^{0,5}]P_{C_2H_4}$	7.6	400—550	41
17	$Cr_2O_3\cdot Al_2O_3$	$r = kP_{H_2}P^{0,5}_{C_4H_8}$	10	220—340	48
18	$MoO_3\cdot Al_2O_3$	$r = kP_{H_2}P^{0,5}_{C_2H_4}$	4	150—450	53
19	$CoO\cdot MoO_3\cdot Al_2O_3$	$r = kP_{H_2}(P_{C_nH_{2n}}/P_{C_nH_{2n+2}})$	22.5—24.5	250—375	57
20	Y_2O_3, La_2O_3, Ho_2O_3	$r = kP_{H_2}$	5—6	—22--22	77

* Experiments conducted in a stream of hydrogen after preliminary adsorption of ethylene, where $\theta_{C_2H_4}$ is the degree of surface coverage with ethylene.

The kinetic results can equally well be explained by the ideas of Eley and Rideal, who assume activation of only one of the reactants (hydrogen or alkene), and by those of Langmuir and Hinshelwood, who regard the interaction of adsorbed species as the limiting stage. In most of the papers cited it is assumed that the catalytically active surface is homogeneous. Nevertheless, the kinetic equations with fractional powers of reactant partial pressures (Table 10) can be explained also by energetic non-uniformity of the active centres.

Sinfelt[9] explained the kinetics of the hydrogenation of ethylene on aluminium oxide by means of Twigg's mechanism[78], involving a stage of interaction between hydrogen adsorbed by van der Waals forces and chemisorbed ethylene:

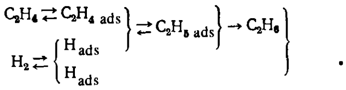
$$C_2H_4 \underset{2}{\overset{1}{\rightleftarrows}} \underset{*}{CH_2}-\underset{*}{CH_2}\ ,$$



$$\underset{*}{CH_2}-\underset{*}{CH_2} + H_2 \underset{4}{\overset{3}{\rightleftarrows}} \underset{*}{\overset{CH_3}{CH_2}} + \underset{*}{H} \xrightarrow{5} C_2H_6\ .$$

A comparative study of the catalytic activity of aluminium oxide towards the hydrogenation of ethylene and of hydrogen–deuterium exchange data suggested[6,7] that activation of ethylene was the limiting stage. Lucchesi et al.[79] detected by infrared spectroscopy the adsorbed ethylene and ethyl assumed in Twigg's mechanism.

Amenomiya and Cvetanovic[80] used thermal desorption to examine the mechanism of the hydrogenation of ethylene on aluminium oxide, and established the presence of two types of adsorption centres, differing in energy of bonding with ethylene. These centres occupy 2.8% of the alumina surface; 60% of them have an activation energy of desorption of 26.8 kcal mole^{-1}, and 40% an activation energy of 36.4 kcal mole^{-1}. Hydrogenation of ethylene occurred more readily on centres of weak adsorption. Ethylene sorbed on them gave with deuterium 1,2-dideuteroethane, which was regarded as indicating hydrogenation by Twigg's scheme. Interaction of the firmly bound ethylene with deuterium gave a mixture of all possible deuteroethanes, which was explained by a mechanism analogous to that suggested by Horiuti and Polanyi[81]:



$$\left.\begin{matrix}\left.\begin{matrix}C_2H_4 \rightleftarrows C_2H_{4\,ads}\\ H_2 \rightleftarrows \left\{\begin{matrix}H_{ads}\\ H_{ads}\end{matrix}\right.\end{matrix}\right\} \rightleftarrows C_2H_{5\,ads}\end{matrix}\right\} \rightarrow C_2H_6\ .$$

This involves a stage of dissociative chemisorption of hydrogen on centres with weak bonding of ethylene, and the formation of ethane via a semi-hydrogenated state.

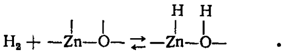
An attempt[7] at a geometrical interpretation of the activation of ethylene on aluminium oxide suggested two possible mechanisms—adsorption of ethylene on two neighbouring aluminium ions in the corundum structure or two-point adsorption on an aluminium ion and an oxygen ion—the length of the aluminium–carbon bond being taken as 1.8 Å in both cases (as in aluminium alkyls). The activation of ethylene on vanadium sesquioxide was assumed[18] to involve adsorption on two vanadium cations.

Interesting results were obtained in studies of the mechanism of the hydrogenation of ethylene and propene on chromic oxide, which showed[19,20] that hydrogenation with deuterium at −78°C did not involve exchange with the hydrogen of the hydrocarbons. The hydrogenation of ethylene with an equimolecular mixture of gaseous hydrogen and deuterium gave[20] ethane, deuteroethane, and dideuteroethanes. Conner and Kokes[20] therefore assume dissociative chemisorption of hydrogen and successive addition of hydrogen atoms. A similar conclusion concerning the mechanism of the hydrogenation of ethylene on cobalt oxide between −78 and 30°C was drawn by some Japanese workers[42] from a study of reaction velocities and product compositions for the four systems

1. $C_2H_4 + H_2$
2. $C_2H_4 + D_2$
3. $C_2H_4 + C_2D_4 + H_2$
4. $C_2H_4 + H_2 + D_2$.

The largest number of investigations on the mechanism of hydrogenation have been made with zinc oxide. Teichner et al.[23-26,82], on the basis of a kinetic study, suggested a mechanism involving interaction between associatively adsorbed ethylene and dissociatively sorbed hydrogen. In contrast to the Horiuti–Polanyi scheme[81], all stages were assumed to be in equilibrium. This scheme was made somewhat more detailed. Catalytic activity was found[23,24] to be independent of the concentration of electrons in the conduction band. This was regarded as indicating a covalent form of chemisorption of hydrogen, as was confirmed also by infrared spectroscopy.

On the basis of infrared spectra Dent and Kokes[28] consider that hydrogen is chemisorbed on coordinatively unsaturated zinc and oxygen ions:



$$H_2 + \text{—}\overset{|}{Zn}\text{—}\overset{|}{O}\text{—} \rightleftarrows \text{—}\overset{H}{\overset{|}{Zn}}\text{—}\overset{H}{\overset{|}{O}}\text{—}\quad .$$

An analogous conclusion was reached by Eischens et al.[83] In the view of the former workers[84] the chemisorption of ethylene is a consequence of π-electron interaction with oxygen ions. Hydrogenation of adsorbed ethylene takes place by the successive addition of hydrogen atoms bound to zinc and oxygen atoms. In the first stage π-adsorbed ethylene becomes detached from oxygen and bound in its semi-hydrogenated form to a zinc atom. The truth of this mechanism is confirmed[85] by the detection, in the infrared spectra, of the compound $Zn-C_2H_5$, which on treatment with hydrogen disappeared at a rate closely similar to the rate of hydrogenation. Krause[86] also supposes that the hydrogenation of ethylene on zinc oxide involves an intermediate semi-hydrogenated form adsorbed on zinc atoms. In contrast to Dent and Kokes[28,84], he assumes that the π-adsorbed ethylene is attached only to zinc atoms.

Table 11. Results for the mechanism of the hydrogenation of ethylene on dysprosium sesquioxide at −55°C.

No.	Initial compound	Reaction products
1	$OH_{surf} + D_2$	HD found only at ⩾ 120°C
2	H_{ads} (w + s)*** + D_2	HD *in minor quantity*
3	H_{ads}(s) + D_2	HD not detected
4	H_{ads}(w + s) + C_2D_4	$C_2H_2D_4$ not detected
5	$C_2D_{4,\,ads} + H_2$	$C_2H_2D_4$
6	$C_2H_4 + H_2$	C_2H_6; $r = 0.46 \times 10^{-9}$*
7	$C_2H_4 + D_2$	99% $C_2H_4D_2$; $r = 0.30 \times 10^{-9}$
8	$C_2D_4 + H_2$	97% $C_2D_4H_2$; $r = 0.42 \times 10^{-9}$
9	$C_2H_4 + C_2D_4$	HD, $C_2H_{4-x}D_x$, $C_2H_{6-x}D_x$—not detected
10	$C_2H_6 + D_2$	HD, $C_2H_{6-x}D_x$—not detected
11	$H_2 + D_2$	HD, $r = 0.38 \times 10^{-9}$
12	$C_2H_4 + H_2 + D_2$ (1.7 : 1 : 1)	47% C_2H_6, 21% C_2H_5D, 32% $C_2H_4D_2$; HD**

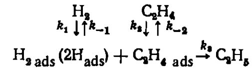
* Rates of reaction for 50% conversion r, mole m^{-2} s^{-1}.

** Detected only after ethylene had been completely hydrogenated.

*** Weakly (w) and strongly (s) adsorbed.

Baranski and Cvetanovic[30] have been able by means of thermal desorption to study the reactivity of five forms of adsorbed hydrogen and two forms of ethylene. They found that only the most weakly bound forms of hydrogen and ethylene take part in hydrogenation. The heat of adsorption of such ethylene is 4–6 kcal $mole^{-1}$. The yellow colour of tungsten oxide does not vanish when ethylene undergoes hydrogenation on the oxide. This suggested[40] that the reaction does not involve atomic hydrogen, and that ethane is formed by Twigg's scheme of interaction of physically adsorbed hydrogen with chemisorbed ethylene.

The mechanism of the hydrogenation of ethylene and propene on rare-earth oxides has been studied by both kinetic and isotope methods. Kinetic investigations by Topchieva et al.[35,38,39] established for the temperature range 130–190°C a mechanism of hydrogenation analogous to that of Polanyi and Horiuti[81], with interaction between the adsorbed alkene and dissociatively chemisorbed hydrogen assumed to be the limiting stage. The mechanism of the low-temperature hydrogenation of ethylene on dysprosium sesquioxide has been examined by isotope and thermal-desorption methods[33,87–89]. A series of reactions which might hypothetically occur in the ethylene–hydrogen–oxide system was studied (Table 11). It is evident for reaction *1* that the hydrogen of surface hydroxyls is not exchanged, and is probably not involved in hydrogenation, under the conditions of catalysis (−55°C). In conformity with reactions *2* and *3* it was established that the two different forms of chemisorbed hydrogen differed in reactivity. These results suggested that firmly sorbed hydrogen played no part in hydrogenation. Reactivity of adsorbed ethylene was shown in reaction *5*. The hydrogenation of ethylene (reactions *7* and *8*) gave only simple addition products. These results indicate absence of dissociative adsorption of ethylene or the ethane formed, which is supported by the investigation of reactions *9* and *10*, when the hydrogen of the hydrocarbons (ethane and ethylene) is not exchanged. Yet in the hydrogenation of ethylene with a mixture of protium and deuterium (reaction *12*) the products of simple addition—ethane and dideuteroethane—were accompanied by deuteroethane C_2H_5D, although H_2-D_2 exchange does not take place under the conditions of hydrogenation. Thus the above investigation shows that the reaction may occur via a semi-hydrogenated form:



$$\begin{matrix} H_2 & & C_2H_4 & & & & \\ {\scriptstyle k_1}\downarrow\uparrow{\scriptstyle k_{-1}} & & {\scriptstyle k_2}\downarrow\uparrow{\scriptstyle k_{-2}} & & & & \\ H_{2\,ads}(2H_{ads}) & + & C_2H_{4\,ads} & \xrightarrow{k_3} & C_2H_{5\,ads} & \xrightarrow{k_4} & C_2H_6, \end{matrix}$$

where stage 3 is irreversible.

Comparison of rates of hydrogenation of ethylene by reactions *6* and *7* revealed a kinetic isotope effect $r_H/r_D = 1.5$. Yet rates of hydrogenation of deuteriated and ordinary ethylene (reactions *6* and *8*) were almost the same. Hydrogen–deuterium exchange and the hydrogenation of ethylene took place at closely similar rates. Furthermore, the activation energies of the two reactions are also equal at ~ 5 kcal $mole^{-1}$. These results suggest that the hydrogenation of ethylene is limited by the activation of hydrogen. Nevertheless, such an assumption does not mean that hydrogenation can take place e.g. by the interaction of chemisorbed hydrogen with physically sorbed ethylene, according to Jenkins and Rideal's mechanism[90]. In the presence of oxide catalysts migration of the double bond in butenes is considerably more rapid than hydrogenation[66,91]. The sequences of catalytic activity of oxides for these reactions were closely similar, which suggested that active centres for activation of the double bond and for hydrogenation were analogous in nature. The mechanism of catalytic hydrogenation should therefore involve both stages—chemisorption of the alkene and chemisorption of hydrogen.

V. CONCLUSION

The information reviewed above shows that oxide catalysts are more complicated than metallic catalysts[1–4]. Work on the latter has developed several methods for obtaining pure and crystallographically uniform surfaces, which has permitted the comparison of metals according to their specific catalytic activity. With oxide catalysts such comparison encounters several difficulties, primarily because of the significant dependence of catalytic activity on conditions of pretreatment. This dependence is not always due solely to the desorption of impurities, as with metals, but is connected with surface oxidation, reduction, and dehydroxylation. Changes in chemical composition are often accompanied by crystallographic changes, which may also influence catalytic activity. This was shown quite clearly by the catalytic properties of oxides of rare-earth metals.

Existing data indicate that, with rise in the temperature of ignition, the activity of an oxide catalyst per square metre of surface increases to a certain limit or else passes through a maximum. The present Reviewers have therefore proposed comparing the "maximum" activities of oxides. However, the effect of ignition temperature on the activity of several oxides has not been studied, so that this approach does not lead to a quantitative comparison of all the catalysts studied.

Qualitative consideration of the data enables oxides to be divided into four groups

(1) very active—Cr_2O_3, La_2O_3, Pr_2O_3, Nd_2O_3

(2) active—Sc_2O_3, Y_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tu_2O_3, Yb_2O_3, Lu_2O_3

(3) moderately active—Co_3O_4, ZnO

(4) relatively inactive—V_2O_3, NiO, Fe_2O_3, Al_2O_3, SiO_2, HfO_2.

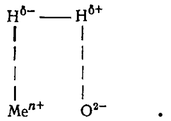
The oxides—ZrO_2, MoO_{2-x}, MgO, MnO, TiO_2, CeO_2, Pr_6O_{11}, and Tb_4O_7—exhibit hardly any activity.

It follows from the above enumeration that hitherto no study at all of catalytic activity has been made on the oxides of gallium, indium, thallium, germanium, tin, lead, niobium, tantalum, antimony, bismuth, tellurium, alkali metals, transuranium elements, and certain other elements intermediate in properties between metals and non-metals. No data are available on the catalytic properties of oxides of the platinum subgroup.

The lack of data for many oxides and the limited study made of others are probably among the main factors preventing any general approaches to the prediction of catalytic activity. The ideas of Dowden, who discussed the energetics of the interaction of an adsorbed particle with a coordinatively unsaturated cation, provide a partial understanding of the variation of activity in oxides of the first transition series. In order to explain the catalytic properties of rare-earth oxides the Reviewers suggested that activities were determined by interaction of an adsorbed molecule with a basic centre. This hypothesis provided a qualitative explanation also of the decrease in activity on passing from oxides to zeolites and silicates.

Thus the development of approaches to the forecasting of catalytic action depends on elucidation of the chemical nature and the structure of the active centre. However, an exact solution of the problem is impossible without elucidation of the chemical nature of the adsorbed species interacting on the surface and the mechanism of the reaction. Despite the abundance of kinetic papers, the mechanism of hydrogenation remains little studied. In experiments with butenes not only can hydrogenation be followed but the main laws governing migration of the double bond, which requires activation of the latter, can be determined. A series of oxides shows analogous variation in activity towards hydrogenation and towards migration of the double bond, which suggests that the active centres for activation of the alkene and for its hydrogenation are the same in nature. Migration of the double bond always occurs under milder conditions and at higher rates than does hydrogenation, which leads to the postulate that activation of hydrogen is the limiting stage. This conclusion has been proved experimentally in a study of the mechanism of the hydrogenation of ethylene on dysprosium oxide.

In spite of the differences in systems studied and in methods of investigation, most workers now consider that the active centre contains an ion-pair comprising a coordinatively unsaturated cation and an oxygen ion, which adsorb a polarised hydrogen molecule:



$$\begin{array}{ccc} H^{\delta-} & \text{—} & H^{\delta+} \\ \vdots & & \vdots \\ Me^{n+} & & O^{2-} \end{array} .$$

This mechanism of activation of the hydrogen molecule suggests that a correlation will exist between catalytic activity and the polarising effect of the ion-pair, which on the whole is apparent. Published information indicates that oxides of trebly charged cations are the most active, whereas those containing doubly and quadruply charged cations either are relatively inactive or do not catalyse hydrogenation at all. It follows also from the above mechanism that easily polarisable substances will act as poisons of catalytic hydrogenation. The relation found between the toxicity of poisons and their ability to abstract a proton supports the hypothesis that catalytic activity is due to an ion-pair. Metals, on the other hand, are not poisoned by most of the substances that are highly toxic to oxides (e.g. water, pyridine, alcohols, ketones).

In the case of alumina, detailed investigation has shown that not all coordinatively unsaturated ions are catalytically active. Centres of catalytic activity may be two adjacent segments of the surface (electron-donating and electron-accepting), respectively aggregates of coordinatively unsaturated cations and of oxygen ions. The diminished catalytic activity of oxides after ignition at high temperatures can be explained in terms of such a model by a redistribution of surface oxygen ions leading to a regular surface structure.

The absence of sufficiently accurate models of the surface for most oxides is currently a serious obstacle to confirming or refining existing views on the nature of active centres.

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Liquid-phase Oxidation of Aldehydes

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Published information on the kinetics and the mechanism of the low-temperature liquid-phase oxidation of various classes of aldehydes–aliphatic, aromatic, unsaturated–is surveyed, and the mechanism of the elementary stages under various conditions –with thermal and photochemical initiation, in the presence of catalysts, in various solvents–is discussed. The mechanism of the concerted oxidation of aldehydes with other organic compounds is also reviewed. Numerical data on these reactions are given in tables. Applications of the oxidation of aldehydes in chemical technology are described. A list of 134 references is included.

CONTENTS

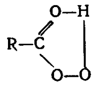
I. INTRODUCTION

The liquid-phase oxidation of organic compounds, the scientific principles of which were developed by Emanuel'[1], is used in many processes of modern chemical technology, in particular in the manufacture of acetic acid and acetic anhydride from acetaldehyde. The oxidation of aldehydes to peroxy-acids, as well as the concerted oxidation of aldehydes and alkenes, shows great practical promise[2]. The oxidation of aldehydes is also of considerable theoretical interest, since they serve as convenient model subjects for study of the kinetics and the mechanism of slow chain reactions with degenerate branching.

The first kinetic studies of the gas-phase oxidation of aldehydes[3,4] belong to the early period when Semenov was establishing the theory of chain reactions[5]. The first and later publications[6,7] give data on the rate of change of pressure and the accumulation of oxidation products of acetaldehyde in the region of slow oxidation and under conditions of cold and hot ignition; the reaction mechanism is also discussed.

Systematic investigations of the kinetics and the mechanism of the gas-phase oxidation of acetaldehyde made by Emanuel' and his coworkers[8-13] were summarised in a review[14]. Oxidation at 125–185°C was found to involve two consecutive chain reactions—(i) oxidation of acetaldehyde with its quantitative conversion into an intermediate hydroperoxide and (ii) interaction of acetyl hydroperoxide with acetaldehyde to form the final products—acetic acid, carbon dioxide and monoxide, ethylene, and water. The surface state of the reaction vessel had a considerable influence on both stages of the process. A discovery of great interest for the modern theory of chain reactions was the existence[9-15] of acyl hydroperoxides (peroxy-acids) in two states with a reversible transition between them as the temperature was varied; the heat of transition was 8 kcal $mole^{-1}$. On rapid cooling ("quenching") of the reacting gaseous mixture of aldehyde and oxygen, the peroxy-acid present passes into a state of enhanced reactivity, apparent in a fall in the ignition temperature when the mixture is reheated after quenching.

The change in the reactivity of peroxy-acids is due to the formation of an intramolecular hydrogen bond with transfer of the acidic proton from one oxygen atom to another.



followed by rearrangement of the valency bonds in the molecule[14,15].

The direct recording of acylperoxy-radicals $AlkCOOO^{\cdot}$ by electron spin resonance has yielded fresh information on the kinetics and the mechanism of the gas-phase oxidation of acetaldehyde at 230–350°C. Peracetic acid is formed by the interaction of acetylperoxy-radicals at $CH_3COOO^{\cdot}$ with acetaldehyde, is the chief intermediate responsible for degenerate chain branching in the oxidation of acetaldehyde, and decomposes mainly heterogeneously on the surface of the reaction vessel.

The oxidation by molecular oxygen of aldehydes in the liquid phase takes place under far milder conditions than in the gas phase. An increasingly large number of papers have appeared on the kinetics of these reactions. There are a few reviews[17-19], but they were published about twenty years ago, and furthermore pay insufficient attention to the elementary mechanism of the process. The present Review covers work on the kinetics and the mechanism of the liquid-phase oxidation of aldehydes by molecular oxygen† completed mainly during recent years. The numerical data obtained in these investigations—bond lengths, equilibrium constants, rate constants and activation energies of individual stages—are given in Tables 1 and 2.

The first experimental confirmation of the radical-chain mechanism of the oxidation of aldehydes was the abnormally high quantum yield (up to 15 000) obtained in the photochemical oxidation of heptanal and benzaldehyde[20].

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† Henceforward the term "oxidation" will be used to imply liquid-phase oxidation by molecular oxygen.

Chain oxidation of aldehydes is effected both thermally and in the presence of various initiators and catalysts. The bonding energy $E_{C(O)-H}$ is relatively small (77–79 kcal mole^{-1}) in aldehydes[21], so that thermal initiation of oxidation is always very significant. In view of the ready oxidisability of aldehydes the value ~80 kcal mole^{-1} seems more justified than 87 kcal mole^{-1} [22,23] (furthermore, it should be the same for different types of aldehydes—acetaldehyde, benzaldehyde, and acrylaldehyde). Values of 74 and 88 kcal mole^{-1} have been published[24] for benzaldehyde and acetaldehyde respectively. It is beyond the scope of the present Review to discuss the accuracy of the values obtained for $E_{C(O)-H}$. If the chain-propagation rate constant k_2 is taken to be a measure of this bonding energy, however, such a large difference between the values for benzaldehyde and acetaldehyde is unjustified. Furthermore, this bonding energy should be smaller in acrylaldehyde than in acetaldehyde[25], which is also inconsistent with the above results[22,23].

Table 1. Length of chain in the oxidation of aldehydes.

Aldehyde	Initiation	Chain length	Temp., °C	Ref.
Benzaldehyde	$h\nu$	15 000	5	20
Heptanal	$h\nu$	4 000	5	17
Acetaldehyde	$h\nu$	10 000	5	1
Benzaldehyde	O_3	50 000	5	1
Butyraldehyde	O_3	200 000	5	1
Decanal	azoisobutyronitrile	8 450	25	1
Benzaldehyde	azoisobutyronitrile	1 050	25	1
Methacrylaldehyde	thermal oxidation	590	26	76
Benzaldehyde	»	450	45	76
Benzaldehyde	»	500	25	38
Heptanal	»	198	43	30
Heptanal	$h\nu$	150	10	35
Isobutyraldehyde	$h\nu$	1 200*	10	35
Isobutyraldehyde	thermal oxidation	250	20	29

* At low partial pressures of oxygen.

II. UNCATALYSED OXIDATION

The general scheme of the liquid-phase oxidation of organic compounds consists[1] of consecutive and parallel elementary stages of chain initiation, propagation, branching, and termination. We shall examine data on each of these stages for the liquid-phase oxidation of aldehydes.

Initiation of Chains

Chains may be initiated in liquid-phase oxidations by the reactions

$$RCHO + O_2 \xrightarrow{k_0} H\dot{O}_2 + RCO^{\cdot}; \quad (1)$$

$$RCHO + RCHO + O_2 \xrightarrow{k_{0'}} H_2O_2 + RCO^{\cdot}; \quad (2)$$

$$RCHO + RCHO \xrightarrow{k_{0''}} 2\,RCO^{\cdot} + H_2 \quad (3)$$

Table 2. Kinetic parameters of elementary stages in the oxidation of aldehydes (subscripts as in text).

Parameter	Aldehyde	Numerical value	Temp., °C	Solvent	Ref.
$k_{0''}$, M^{-2} s^{-1}	decanal	$1.6\cdot10^{3}\exp(-11\,600/RT)$	5—20	n-decane	28
	»	$2.5\cdot10^{-6}$ *	20	»	
	acetaldehyde	$2.7\cdot10^{5}\exp(-17\,200/RT)$	60—100	benzene	26
	»	$5.3\cdot10^{-8}$ *	20	»	
	benzaldehyde	$6.3\cdot10^{7}\exp(-16\,400/RT)$	30—50	acetic acid	32
	»	$4\cdot10^{-5}$ *	20	»	
	decanal	$8\cdot10^{4}\exp(-15\,600/RT)$	5—20	none	27
	»	$2\cdot10^{-7}$ *	20	»	
	isobutyraldehyde	$8.7\cdot10^{-8}$	20	chlorobenzene	29
$k_{0'''}$, M s^{-1}	benzaldehyde	$2.1\cdot10^{-5}$	43	*o*-dichlorobenzene	30
	isobutyraldehyde	$6.3\cdot10^{8}\exp(-19\,500/RT)$	10—30	chlorobenzene	29
	»	10^{-7} *	43	»	
	methylacrylaldehyde	$2.9\cdot10^{4}\exp(-17\,300/RT)$	−17÷+30	none	41
	»	$2.9\cdot10^{-8}$ *	43	»	
	»	$3.8\cdot10^{2}\exp(-13\,600/RT)$	26—45	»	76
	»	$1.5\cdot10^{-7}$ *	43	»	
	ethylacrylaldehyde	$10^{4}\exp(-15\,700/RT)$	−17÷+30	»	41
	propylacrylaldehyde	$6.3\cdot10^{4}\exp(-17\,500/RT)$	−17÷+30	»	41
	isopropylacrylaldehyde	$2.7\cdot10^{3}\exp(-14\,000/RT)$	−17÷+30	»	
	crotonaldehyde	$1.75\cdot10^{4}\exp(-14\,900/RT)$	−14÷+20	»	31
	»	$7\cdot10^{-7}$ *	43	»	
	acrylaldehyde	$6.3\cdot10^{-2}$***	40	benzene	89
k_2, M^{-1} s^{-1}	benzaldehyde	$5\cdot10^{4}\exp(-1\,800/RT)$	5—20	n-decane	28
	»	$1.9\cdot10^{3}$ *	0	»	
	»	$1.2\cdot10^{4}$	0	chlorobenzene	39
	acetaldehyde	$1.6\cdot10^{3}$	0	»	
	heptanal	$3.9\cdot10^{3}$	0	»	
	octanal	$3.3\cdot10^{3}$	0	»	
	cyclohexanal	$1.4\cdot10^{3}$	0	»	
	trimethylacetaldehyde	$3.4\cdot10^{3}$	0	»	
	decanal	$1.4\cdot10^{6}\exp(-4\,200/RT)$	5—20	none	27
	»	$6.3\cdot10^{2}$ *	0	»	
	isobutyraldehyde	$3.5\cdot10^{5}\exp(-6\,000/RT)$	10—30	chlorobenzene	29
	»	5.5 *	0	»	
	methylacrylaldehyde	$9.3\cdot10^{3}\exp(-4\,300/RT)$	−17÷+30	none	41
	»	3.5 *	0	»	
	ethylacrylaldehyde	$4.6\cdot10^{4}\exp(-5\,000/RT)$	−17÷+30	»	
	propylacrylaldehyde	$2.7\cdot10^{3}\exp(-3\,500/RT)$	−17÷+30	»	
	isopropylacrylaldehyde	$7.3\cdot10^{3}\exp(-9\,300/RT)$	−17÷+30	»	
	methylacrylaldehyde	$4.1\cdot10^{3}\exp(-4\,600/RT)$	26—45	»	76

Parameter	Aldehyde	Numerical value	Temp., °C	Solvent	Ref.
E_2, kcal mole^{-1}	benzaldehyde	2.3	25—50	benzene	36
	»	1.0	42—85	o-dichlorobenzene	30
	»	6.8 **	20—35	acetic acid	38
	»	7.8 **	20—45	»	37
	heptanal	4.0	10—30	none	35
k_3, , s^{-1}	benzaldehyde	$6.3\cdot10^{12}\exp(-30\,000/RT)$	60—70	benzene	47
	acetaldehyde	$10^{14}\exp(-32\,000/RT)$	75—95	toluene	46
k_6, M^{-1} s^{-1}	benzaldehyde	$2.1\cdot10^{8}$	5	n-decane	28
	»	$7.5\cdot10^{8}$	0	chlorobenzene	39
	acetaldehyde	$2.6\cdot10^{7}$	0	»	
	heptanal	$2.65\cdot10^{7}$	0	»	
	octanal	$2.6\cdot10^{7}$	0	»	
	cyclohexanal	$4.8\cdot10^{6}$	0	»	
	trimethylacetaldehyde	$4.0\cdot10^{6}$	0	»	
	decanal	$7.5\cdot10^{6}$	5	n-decane	27
	»	$3.4\cdot10^{6}$	5	»	28
	methylacrylaldehyde	$2.4\cdot10^{4}\exp(-1\,900/RT)$	$-17\div+30$	none	41
	»	$7.5\cdot10^{2}$ *	0	»	
	»	$1.3\cdot10^{5}\exp(-900/RT)$	26—45	»	76
	»	$1.5\cdot10^{4}$ *	0	»	
	ethylacrylaldehyde	$8.8\cdot10^{4}\exp(-1\,000/RT)$	$-17\div+30$	»	41
	propylacrylaldehyde	$5.4\cdot10^{5}\exp(-1\,200/RT)$	$-17\div+30$	»	
	isopropylacrylaldehyde	$2.5\cdot10^{6}\exp(-2\,800/RT)$	$-17\div+30$	»	
	crotonaldehyde	$1.7\cdot10^{5}\exp(-1\,600/RT)$	$-14\div+20$	»	31
	»	10^{4} *	0	»	
	isobutyraldehyde	$9.5\cdot10^{7}\exp(-4\,100/RT)$	10—30	chlorobenzene	29
	»	$5.5\cdot10^{4}$ *	0	»	
k_7, s^{-1}	acetaldehyde	$10^{10}\exp(-5\,000/RT)$	40—70	benzene	42
K_9, M	acetaldehyde	$3.4\cdot10^{-1}$ **	25	acetic acid	60
	»	$2.7\cdot10^{-1}$	25	»	58
	»	$2.6\cdot10^{-1}$ **	25	»	
	»	$1.6\cdot10^{3}\exp(-5\,500/RT)$	0—25	toluene	59
	»	$1.6\cdot10^{-1}$ *	25	»	59
	acrylaldehyde	1.3 **	30	none	55
k_{-9}, s^{-1}	acetaldehyde	$5\cdot10^{5}\exp(-12\,000/RT)$ **	5—25	acetic acid	94
$k_{9'}$, s^{-1}	acetaldehyde	$1.25\cdot10^{10}\exp(-19\,000/RT)$	$-20\div0$	ethyl acetate	61
	»	$1.6\cdot10^{-4}$ *	25	»	
	»	$6.7\cdot10^{-5}$	20	toluene	62
	»	$1.1\cdot10^{-4}$	25	acetaldehyde	49
$k_{9''}$, M^{-1} s^{-1}	benzaldehyde	$2.1\cdot10^{3}\exp(-10\,000/RT)$	42—85	o-dichlorobenzene	30
	»	$1.3\cdot10^{-4}$ *	30	»	
	»	$2.8\cdot10^{-4}$	29	acetic anhydride	66
	»	$10^{5}\exp(-11\,900/RT)$	30—45	acetic acid	37
	»	$2.5\cdot10^{-4}$ *	30	»	37
E_{-9}, kcal mole^{-1}	acetaldehyde	13.0	25	toluene	59
$E_{9'}$, kcal mole^{-1}	acetaldehyde	15.0			17
K_{15}, M^{-2}	benzaldehyde	$6.8\cdot10^{12}\exp(-13\,300/RT)$	20—45	acetic acid	37
k_{15}, s^{-1}	benzaldehyde	$2.3\cdot10^{4}\exp(-7\,500/RT)$	20—45	acetic acid	37

* Calculated from authors' data.
** Cobalt acetate as catalyst.
***Copper and iron phthalocyanines as catalyst.

From published bonding energies in reactant and product molecules the negative heats of reactions (1)–(3) for aldehydes having $E_{C(O)-H} \simeq 80$ kcal mole^{-1} can be estimated as 35, 20, and 55 kcal mole^{-1} respectively. Thus the termolecular reaction (2) is energetically the most favourable. In experimental kinetic investigations, however, various workers have observed both bimolecular and termolecular initiation. Reaction (2) has been established in the oxidation of acetaldehyde[26], decanal[27,28], and benzaldehyde[34]; initiation by reaction (3) occurs in the oxidation of isobutyraldehyde[29], benzaldehyde[30], α-alkylacrylaldehydes, and crotonaldehyde[31]. The pre-exponential factor of reaction (2) for saturated aldehydes is 10^3–10^5 M^{-2} s^{-1}; that of reaction (3) for unsaturated aldehydes is 10^3–10^4 M^{-1} s^{-1}, with E = 15–17 kcal mole^{-1}. In the oxidation of isobutyraldehyde initiation occurs mainly by reaction (3), the pre-exponential factor is 6×10^8 M^{-1} s^{-1}, and E = 19.5 kcal mole^{-1} (calculated from the Reviewers' experimental results).

The rate constant of initiation in the oxidation of benzaldehyde exceeds those for aldehydes of other types by factors of 10^2.[30] Available experimental results do not enable any unambiguous relation to be established between the structure of an aldehyde and the mechanism of the initiation of oxidation chains.

Initiation of the oxidation of aldehydes may occur also by the reaction[33]

$$RCH_2CHO + O_2 \rightarrow R\dot{C}HCHO + HO_2^{\cdot} \tag{4}$$

whose negative heat of reaction should be 25–30 kcal mole^{-1}. The radical $\cdot$CHR.CHO may give rise to formic acid, small quantities of which are present among the products of the oxidation of aldehydes containing two or more carbon atoms. It is formed as a result of decomposition of the hydroperoxide:

$$\mathrm{RCH(OOH){-}CHO \rightarrow OH^{\cdot} + RCH(\dot{O}){-}CHO \rightarrow RCHO + HCO^{\cdot};}$$
$$\mathrm{HCO^{\cdot} + OH^{\cdot} \rightarrow HCOOH.}$$

Abstraction of hydrogen from a methylene or a methyl group in an aldehyde is promoted by the presence of a catalyst[34].

Chain Propagation

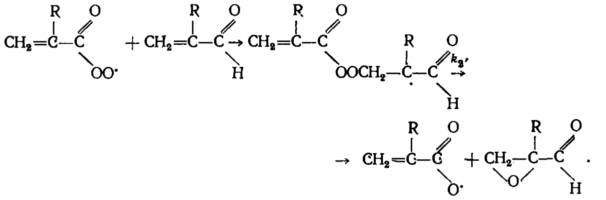
A chain is propagated by addition of an oxygen molecule to an acyl radical and abstraction of hydrogen from an aldehyde molecule by the acylperoxy-radical formed:

$$\mathrm{RCO^{\cdot} + O_2 \xrightarrow{k_1} RCOOO^{\cdot};} \quad (5)$$
$$\mathrm{RCOOO^{\cdot} + RCHO \xrightarrow{k_2} RCOOOH + RCO^{\cdot}.} \quad (6)$$

Reaction (5) is exothermic (~ 20 kcal mole^{-1}) and is very rapid, with rates of 10^7–10^8 M^{-1} s^{-1} and almost zero activation energy (E_1 = 2.0 ± 1.5 kcal mole^{-1} was given[35] for the oxidation of heptanal). Reaction (6), leading to the formation of peroxy-acids, is also exothermic, but less strongly so than reaction (5). The activation energy E_2 = 4–6 and 3–5 kcal mole^{-1} respectively for saturated aliphatic[27,29,35] and unsaturated[31] aldehydes, the corresponding pre-exponential factors being 10^5–10^6 and 10^3–10^4 M^{-1} s^{-1}, so that rates of chain propagation are higher in the oxidation of saturated aldehydes (by factors of 10–10^2). In the oxidation of benzaldehyde E_2 has the values 1–2 and 6–8 kcal mole^{-1} in the absence of a catalyst[28,30,36] and in the presence of cobalt acetate respectively[37,38]; the pre-exponential factor is 50 000 M^{-1} s^{-1}.[28] Values differing almost tenfold have been given[28,39] for the rate constant k_2 for benzaldehyde, the lower of which is fivefold the rate constant k_2 for decanal[27] and coincides with those obtained[39] for saturated aliphatic aldehydes. According to these measurements[39] k_2 for benzaldehyde is almost tenfold those for aliphatic aldehydes, e.g. acetaldehyde. Thus values of k_2 determined by different workers vary by almost a whole order of magnitude. The lower rate of chain propagation (and hence of the overall oxidation) with unsaturated aldehydes can be explained[25] by features of the intermediate complex formed in reaction (6) with compounds having conjugated double bonds. The hypothesis that reaction (6) involves the intermediate complex $[\mathrm{RO_2^-} : \dot{\mathrm{H}}\ \overset{+}{\mathrm{R}}{}']$ was put forward[40] for the oxidation of substituted aromatic ethers.

It can now be accepted that the rates of oxidation of unsaturated aldehydes are substantially lower than those of the corresponding saturated aldehydes[31]. This is probably due not only to different rates of chain propagation but also to the rate of initiation.

The mechanism of the oxidation of unsaturated aldehydes (α-alkylacrylaldehydes) involves not only reaction (6) but also another chain-propagating reaction, between an acylperoxy-radical and the double bond of the aldehyde[41]:



(7)

Occurrence of this reaction is supported by the presence of α-alkylepoxypropionaldehydes among the oxidation products from α-alkylacrylaldehydes.

Chain propagation in the oxidation of aldehydes may involve not only RCOOO$\cdot$ radicals but also acyloxy-radicals RCOO$\cdot$ formed by cleavage of peroxy-acids at the RCOO–OH bond:

$$\mathrm{RCOO^{\cdot} + RCHO \xrightarrow{k_{2''}} RCOOH + RCO^{\cdot}.} \quad (8)$$

This reaction, leading to the formation of acids, competes with decomposition of the acyloxy-radicals[42,43], which occurs at 20–70°C with considerable rapidity. At sufficient aldehyde concentrations reaction (8) predominates. This is confirmed by experiments on the decomposition of acetyl peroxide in the presence of 3 M acetaldehyde in benzene solution at 70°C, in which the yield of acetic acid per mole of peroxide decomposed exceeded fourfold the yield of carbon dioxide[44]. The rate constant $k_{2''}$ was not estimated.

Branching of Chains

Degenerate branching of chains probably plays a less significant role in the liquid-phase oxidation of aldehydes than in the oxidation of hydrocarbons. This may be deduced from a comparison of the rate of thermal initiation by reaction (2) with the rate of radical decomposition of peroxy-acids

$$\mathrm{RCOOOH \xrightarrow{k_3} RCOO^{\cdot} + OH^{\cdot}.} \quad (9)$$

The activation energy of reaction (9) for peracetic and perbenzoic acids is[45–47] 30–33 kcal mole^{-1} (which corresponds to the energy of the oxygen–oxygen bond in a peroxy-acid). The pre-exponental factor is 10^{13}–10^{14} s^{-1}, which is fully consistent with the unimolecular reaction (9): the factor would have been considerably smaller for induced decomposition of the peroxy-acids. The rate constant of reaction (9) at 70°C is $k_3 = 10^{13} = \exp(-30\,000/RT) = 10^{-6}$ s^{-1}. When the concentration of the peroxy-acid is 0.2 M, the rate of degenerate chain branching by reaction (9) is 2×10^{-7} M s^{-1}. Yet the rate of chain initiation by reaction (2) in the oxidation of acetaldehyde under these conditions is 1.05×10^{-6} M s^{-1} [48] (or 3.6×10^{-7} M s^{-1} [44]). Thus the rate of degenerate branching (9) is even somewhat smaller than the rate of initiation (2). A similar conclusion was reached[30] from a comparison of the rates of decomposition of perbenzoic acid and of thermal initiation of chains in the oxidation of benzaldehyde. Peroxy-acids can evidently decompose also by a bimolecular reaction

$$\mathrm{2RCOOOH \rightarrow RCOOO^{\cdot} + RCO^{\cdot} + H_2O}$$

analogous to the reaction for hydroperoxides. The rate constant of this reaction for peroxy-acids has not been measured. In the oxidation of hydrocarbons $k_3 = 10^6$ M^{-1} s^{-1} at 40–60°C.[1]

A possibility in the low-temperature oxidation of aldehydes is that chain branching may occur by breakdown of an addition product of peroxy-acid and aldehyde (henceforward termed for brevity an "adduct")[49]. Addition of a small quantity of the adduct (1-hydroxyethyl peracetate) to a solution of acetaldehyde in acetic acid eliminated the induction period and accelerated considerably oxidation of the aldehyde at 18°C. Under the experimental conditions this peroxy-compound broke down mainly by a molecular mechanism, but a small fraction (~0.1%) of the peroxide decomposed into radicals. Unfortunately, the paper did not contain sufficient data for the rate of initiation to be estimated, and only the actual fact of the initiating action of the adduct at low temperatures can be established. With rise in temperature the importance of this mode of degenerate chain branching will probably diminish because of a shift in the adduct equilibrium towards formation of the corresponding peroxy-acid and the aldehyde.

Termination of Chains

In the liquid-phase oxidation of aldehydes termination is effected by the recombination of radicals:

$$RCO^{\cdot} + RCO^{\cdot} \xrightarrow{k_4} \text{Molecular products} \qquad (10)$$

$$RCO^{\cdot} + RCOOO^{\cdot} \xrightarrow{k_5} \text{Molecular products} \qquad (11)$$

$$RCOOO^{\cdot} + RCOOO^{\cdot} \xrightarrow{k_6} \text{Molecular products} \qquad (12)$$

The relative rates of these reactions are directly dependent on the concentration of dissolved oxygen: at low concentrations termination occurs predominantly by reaction (10); with excess of oxygen, because of the higher rate of reaction (5) than of (6), the system contains almost solely RCOOO· radicals, the only termination reaction is (12), and the rate of oxidation becomes independent of the oxygen concentration. The dependence of the rate of oxidation on the concentrations of the starting materials is given by the formula

$$W = W_{\infty}\left[1 + \frac{k_5}{k_6}\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]} + \frac{k_4}{k_6}\left(\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]}\right)^2\right]^{-1/2},$$

where

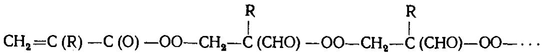
$$W_{\infty} = \frac{k_2}{k_6^{1/2}}[\mathrm{RH}]W_i^{1/2},$$

in which W_i is the rate of initiation.

Experimental results for the dependence of the rate of oxidation of acetaldehyde in benzene solution on the concentration of dissolved oxygen[50] are well reproduced by this formula. The rate becomes independent of the oxygen concentration when the latter reaches 0.2 M.[50]

A similar dependence of reaction velocity on partial oxygen pressure was obtained[35] for the oxidation of benzaldehyde. At low oxygen concentrations, when $[C_6H_5CHO]/p_{O_2} \geqslant 0.01$ M mm^{-1}, the rate of reaction is linearly dependent on the partial pressure, but with ratios $\leqslant 0.002$ M mm^{-1} (which corresponds to 0.1 M oxygen) it is independent of the oxygen pressure. The intermediate range of $[C_6H_5CHO]/p_{O_2}$ ratios is characterised by a fractional kinetic order with respect to molecular oxygen. It is interesting that the limiting oxygen concentration (0.1–0.2 M) at which the rate of oxidation of the aldehyde ceases to depend on the oxygen pressure far exceeds the values usual for the oxidation of hydrocarbons (e.g. $\sim 10^{-5}$ M for ethyl linoleate[51] and tetrahydronaphthalene[1]). An explanation offered[50] for this was that the rate constant of reaction (10), in competition with reaction (5), is greater for acyl radicals RCO· than for alkyl radicals R·.

In practice the oxidation of aldehydes is almost always conducted under conditions such that chain termination occurs solely by reaction (12). It was usually considered that no activation energy was involved, but values E_6 = 1–3 and 4 kcal mole^{-1} were obtained in the oxidation of unsaturated aldehydes[31] and of isobutyraldehyde[29] respectively. The pre-exponential factors of reaction (12) are 10^4–10^5, 10^6–10^7, and 10^8 M^{-1} s^{-1} for unsaturated aldehydes, saturated aliphatic aldehydes, and benzaldehyde. The difference in these factors for different groups of aldehydes remains difficult to understand (especially the low values for unsaturated aldehydes[31]). The activation energy of chain termination also requires further experimental study. In the oxidation of unsaturated aliphatic aldehydes[41] termination may occur also by means of the radical $CH_2:\dot{C}R.CO.O.O.CH_2.CR(CHO)^{\cdot}$, whose transformation leads to formation of the polyperoxide



$$CH_2{=}C(R){-}C(O){-}OO{-}CH_2{-}\overset{\overset{\displaystyle R}{|}}{C}(CHO){-}OO{-}CH_2{-}\overset{\overset{\displaystyle R}{|}}{C}(CHO){-}OO{-}\cdots$$

Only fragmentary data are available on the nature of the molecular products of chain termination in the oxidation of aldehydes. For example, butane-2,3-dione, formed by the recombination of acyl radicals, has been identified[52] among the oxidation products from acetaldehyde in benzene solution with low concentrations of oxygen at 70°C. The oxidation of benzaldehyde in acetic acid[53] yields benzoyl peroxide, perhaps because of chain termination by reaction (12). Acetic anhydride among the oxidation products of acetaldehyde was attributed[54] to chain termination by the reaction RCO· + RCOO·, but no experimental results were given in support.

Because of the great length of the chain, products of termination are formed in very small quantities, and cannot always be identified. Table 1 gives data on the length of the chain in the oxidation of aldehydes.

Mechanism of Formation of Molecular Products

Molecular products may be formed both from the radicals responsible for the chain process and from valency-saturated molecules. The RCOO· radicals formed at the stage of degenerate branching by decomposition of peroxy-acids readily undergo decarboxylation:

$$RCOO^{\cdot} \xrightarrow{k_7} R^{\cdot} + CO_2. \qquad (13)$$

However, if an aldehyde is present in the system, competition by reaction (8) noted above results in formation of a far smaller quantity of carbon dioxide than from decomposition of the peroxy-acid in an inert solvent. Thus addition of acetaldehyde in the decomposition of acetyl peroxide in benzene solution at 70°C lowered the yield of carbon dioxide from 80 to only 25 mole % of the peroxide decomposed[44].

Carbon dioxide may be formed also from acylperoxy-radicals:

$$RCOOO^{\cdot} \rightarrow RO^{\cdot} + CO_2. \qquad (14)$$

However, no experimental results have been published on this reaction. It has merely been postulated[55] among other hypothetical reactions possible in the oxidation of acrylaldehyde.

The formation of carbon dioxide in the oxidation of acetaldehyde by air was studied[56] in benzene solution under 50 atm at 60°C. Hardly any carbon dioxide was formed in a glass reaction vessel, which indicated that reaction (14) occurs predominantly by a heterogeneous mechanism. This is confirmed by the increased yield of carbon dioxide produced by increasing the ratio of surface to volume of the reaction vessel.

Carbon monoxide is probably formed by the decomposition of acyl radicals[57]:

$$RCO^{\cdot} \xrightarrow{k_8'} CO + R^{\cdot} \qquad (15)$$

Acids are formed in the oxidation of aldehydes as a result of reaction between the aldehyde and the peroxy-acid:

$$\mathrm{RCOOOH} + \mathrm{RCHO} \overset{K_9}{\rightleftarrows} \mathrm{X}, \qquad (16)$$

$$\mathrm{X} \xrightarrow{k_{9'}} 2\,\mathrm{RCOOH}. \qquad (17)$$

It was suggested[58] that this reaction involves the intermediate formation of a compound X (an "adduct") having the structure R.CH(OOH)–O.CO.R. A detailed study was made of the kinetics of the formation of acetic acid in the oxidation of acetaldehyde[28]. The experimental results were fully described by the kinetic scheme involving intermediate formation of the adduct. The equilibrium constant K_9 for acetaldehyde is 0.1–0.3 M at 25°C [55,58-60], and E_9 = 5.5 kcal mole^{-1}.[59] Values of the rate constant $k_{9'}$ obtained by several workers[49,61,62] for decomposition of the adduct showed satisfactory agreement. Activation energies $E_{9'}$ = 19 and 15 kcal mole^{-1} were obtained[61,17]. The many independent determinations and the good agreement among the results indicate that K_9 and $k_{9'}$ may well be among the most reliably determined elementary constants in the oxidation of aldehydes.

There is considerable disagreement as to which classes of aldehydes form an adduct. This was regarded[55,58,63,64] as occurring only in the oxidation of aliphatic aldehydes, whereas aromatic aldehydes underwent direct oxidation

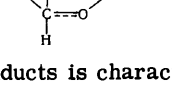
$$\mathrm{RCOOOH} + \mathrm{RCHO} \xrightarrow{k_{9''}} 2\mathrm{RCOOH}. \qquad (18)$$

Infrared spectroscopy did not reveal formation of an adduct in the oxidation of benzaldehyde[65], but the opposite conclusion was reached from kinetic[66,67] and spectroscopic[68] data. Formation of an adduct was stated[25,69] to occur in the oxidation of acrylaldehyde, but the same authors gave a scheme[57] from which the adduct was absent. The present Reviewers consider that unambiguous evidence of the existence of an adduct would be its isolation in pure form from the reaction mixture at low temperatures. This method was adopted[70] in studying the oxidation of acetaldehyde and butyraldehyde. Isolation of an adduct had been achieved earlier[71] in the oxidation of another saturated aliphatic aldehyde, undecanal. The question of the formation of an adduct in the oxidation of aromatic and unsaturated aliphatic hydrocarbons cannot be regarded as settled.

In the early investigations by infrared spectroscopy[72] a hydroperoxide form of adduct was assumed to be present. Examination of the nuclear magnetic resonance spectra of products of the low-temperature oxidation of acetaldehyde led to the conclusion[70] that the adduct could have two possible structures

$$\underset{(a)}{\mathrm{CH_3C(O)}\text{—}\mathrm{OO}\text{—}\mathrm{CH(OH)}\text{—}\mathrm{CH_3}};\quad \underset{(b)}{\mathrm{CH_3}\text{—}\overset{\mathrm{O—O}}{\mathrm{C}}\text{—}\mathrm{O}\text{—}\mathrm{CH(OH)}\text{—}\mathrm{CH_3}},$$

of which (*a*) was the more probable. Almost all authors who postulated formation of an adduct during oxidation assumed a similar structure. Kinetic study of the decomposition of adducts from acetaldehyde and butyraldehyde established[70] that decomposition occurred mainly by a molecular mechanism via a cyclic intermediate complex of type



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The presence of adducts is characteristic of the low-temperature of oxidation of acetaldehydes. The quantity of adduct in the mixture is considerably diminished by raising the temperature merely to 10–20°C, and the main oxidation product becomes acetic acid[73].

Carboxylic acids may be formed in the oxidation of aldehydes not only by breakdown of an adduct but also directly from peroxy-acids as a result of their molecular decomposition:

$$\mathrm{RCOOOH} \rightarrow \mathrm{RCOOH} + \frac{1}{2}\mathrm{O_2} \ . \qquad (19)$$

This reaction was postulated on the basis of results obtained by several workers[26,30,74,75] in kinetic studies of the decomposition of peroxy-acids. An almost 100% yield of carboxylic acid was obtained based on the peroxy-acid decomposed, and evolution of molecular oxygen was observed. The fact that inhibitors and initiators of radical reactions had no effect on the decomposition of peroxy-acids was further evidence of molecular decomposition. The activation energy of reaction (19), 16–24 kcal mole^{-1}, is less than for the radical decomposition of peroxy-acids. Decomposition of peracetic acid is a first-order reaction with respect both to this acid and to acetic acid[76].

III. PHOTOCHEMICAL OXIDATION—INITIATION OF CHAINS

In the photochemical oxidation of aldehydes the reaction mixture is usually exposed to ultraviolet radiation of wavelength 2500–4000 Å. On absorbing a quantum the aldehyde molecule passes into an excited singlet state S_1, from which a radiationless transition can occur to a metastable triplet state T_1.

At sufficient aldehyde concentrations the excited molecules are deactivated by interaction with aldehyde molecules in the ground state, while free radicals are produced, and initiate the chain process. Since the lifetime of the T_1 state greatly exceeds that of S_1, radicals are most probably formed by autodeactivation of the T_1 state. In the gas phase, e.g. with benzaldehyde, the lifetimes of S_1 and T_1 states are 1.6 μs and 2 ms respectively[77]. In the photochemical oxidation of benzaldehyde the initiation of chains was regarded[78] as resulting mainly from reaction between an aldehyde molecule in the triplet state and an unexcited molecule:

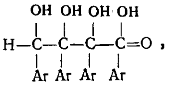
$$\mathrm{C_6H_5CHO} + h\nu \rightarrow \mathrm{C_6H_5\dot{C}H\text{—}\dot{O}};$$

$$\mathrm{C_6H_5\dot{C}H\text{—}\dot{O}} + \mathrm{C_6H_5CHO} \rightarrow \mathrm{C_6H_5\dot{C}O} + \mathrm{C_6H_5\dot{C}HOH}.$$

This quite widely held view on the mechanism of chain initiation in the photochemical oxidation of aldehydes[79,80] is contradicted by results obtained at low partial pressures of oxygen (54–450 mm) in an investigation[81] of the oxidation of decanal in decane solution with λ = 3130 Å at 10°C. It was concluded[81] that at low oxygen pressures radicals are initiated mainly by reaction between an oxygen molecule in an S_1 state and an unexcited aldehyde molecule. At higher pressures both S_1 and T_1 are involved in radical formation.

It has been recommended that special additives which readily produce free radicals under the influence of light, e.g. butane-2,3-dione, be introduced in the oxidation of heptanal[35], in order to improve the efficiency of photochemical initiation. On absorption of a quantum (λ = 4358 Å) the dione passes into an excited singlet state, which is converted almost quantitatively into a triplet state. The latter is deactivated mainly by reaction with molecular oxygen, and free radicals are formed. With this method of initiation the rate of generation of chains is constant during oxidation.

Photochemical initiation is an efficient method of intensifying oxidation which finds practical application for obtaining oxidation products of aldehydes. In photochemical oxidation the above reactions of chain termination (10)–(12) are probably accompanied by destruction of radicals on the molecules of certain oxidation products. This may explain in particular why the oxidation of aldehydes gradually slows down with time. Thus it was suggested[82] that the compound



$$\mathrm{H{-}C(OH)(Ar){-}C(OH)(Ar){-}C(OH)(Ar){-}C(OH)(Ar){=}O}$$

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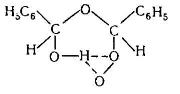
formed in the liquid-phase photolysis of benzaldehyde, may act as an inhibitor. Preliminary photolysis of heptanal in an oxygen-free medium lowers the rate of a subsequent oxidation[17]. The oxidation of benzaldehyde slows down at a time when considerable quantities of aldehyde are still present in the mixture[30]. Some quantities (1–2%) of salicylaldehyde and phenol, which are inhibitors, have been shown to be present.

A study of the photochemical oxidation of benzaldehyde in the presence of quinol as inhibitor established that the absorption of one quantum by an aldehyde molecule initiates only one reaction chain[78]. Since the act of initiation produces two radicals, $C_6H_5CO\cdot$ and $C_6H_5CH(OH)\cdot$, this result was explained by the destruction of one of the radicals according to the scheme

$$\mathrm{C_6H_5\dot{C}HOH + C_6H_5CHO \rightarrow C_6H_5CH(OH){-}O{-}\dot{C}H{-}C_6H_5 \xrightarrow{+O_2}}$$
$$\mathrm{\rightarrow C_6H_5CH(OH){-}O{-}CH(O\dot{O}){-}C_6H_5}\ .$$

It is assumed that the rate of this reaction in pure benzaldehyde will be comparable with the rate of the reaction between $C_6H_5CH(OH)\cdot$ and molecular oxygen. The resulting radical tends to form intramolecular hydrogen bonds



which is responsible for its characteristic reactivity.

The phenomenon of autoinhibition noted in papers on photochemical oxidation has been observed also in the thermal oxidation of benzaldehyde. This can be attributed both to the inhibiting effect of certain oxidation products and to possible deactivation of the catalyst in the later stages of catalytic oxidation[83]. Thus phenol has been detected in the thermal oxidation of benzaldehyde[66], and is formed as secondary product of the reaction between benzaldehyde and perbenzoic acid[63], its quantity being greater the more strongly electron-donating is the *para*-substituent in a substituted benzaldehyde.

IV. CATALYSED OXIDATION

Catalysts, mainly compounds of metals of variable valency, are widely employed to increase the rate and the selectivity of the oxidation of aldehydes. Published information relates mainly to homogeneous catalysts, but considerable interest has recently been taken in the use of heterogeneous catalysts. Introduction of a catalyst leads to a significant change in the mechanism of the process.

Initiation of Chains

Initiation may result from interaction of the catalyst with a molecule of a peroxy-acid or an aldehyde, which can be represented schematically

$$M^{n+} + \mathrm{RCOOOH} \xrightarrow{k_{3'}} M^{(n+1)+} + \mathrm{OH}^- + \mathrm{RCOO}^{\cdot}; \tag{20}$$

$$M^{(n+1)+} + \mathrm{RCHO} \xrightarrow{k_{3''}} M^{n+} + \mathrm{H}^+ + \mathrm{RCO}^{\cdot}; \tag{21}$$

$$M^{(n+1)+} + \mathrm{RCOOOH} \xrightarrow{k_{3'''}} M^{n+} + \mathrm{H}^+ + \mathrm{RCOOO}^{\cdot}. \tag{22}$$

Reaction (20), involving oxidation of the catalyst ion, is usually far more rapid than (21) and (22). Its rate depends on the nature of the metal ion[38,84], but for the most commonly used homogeneous catalysts—cobalt, copper, and manganese salts—its rapidity leads to the presence of the catalyst ions almost entirely in the state of higher valency during the reaction. The oxidised form of the ion may generate free radicals as a result of reaction with the initial aldehyde or with the peroxy-acid. The rates of these reactions were measured[38], and the rate of (21) for benzaldehyde was determined by independent measurements in a mixture of acetic and sulphuric acids. The rate constant obtained agreed satisfactorily with that of chain initiation determined from the consumption of inhibitor during the oxidation of benzaldehyde.

From this it was concluded that reaction (21) was responsible for chain initiation in the oxidation of benzaldehyde in the presence of a catalyst. This view was fairly widespread in the literature until quite recently, but it can hardly be accepted as soundly based. Firstly, the consumption of inhibitor can be related only to the total rate of interaction with radicals, whereas free radicals are formed primarily by the uncatalysed reaction (2) or (3). After a certain quantity of peroxy-acid has accumulated, radicals are formed by reactions (21) and (22). Considerable inaccuracy is due also to the fact that the measured[38] rate of reaction (21) is far too high, because the rate constant obtained in sulphuric-acid medium exceeds significantly its value in an inert solvent[37]. Moreover, the same work[38] gave $k_{3''} = 0.05$ M s^{-1}, and the rate constant of reaction (22) as 0.8 M s^{-1}, which contradicts the authors' statement that reaction (21) predominated in the initiation of chains. Measurements of the rates of reactions (21) and (22) in acetic-acid medium during the oxidation of benzaldehyde gave values of 8×10^{-11} and 7×10^{-7} M s^{-1} at 30°C.[37] The rate of the uncatalysed initiation (2), determined under the same conditions for comparison, was 1.3×10^{-8} M s^{-1}. A similar ratio of rates of (21) and (22) has been observed[85] in the oxidation of *p*-tolualdehyde.

Thus the main reaction responsible for the formation of free radicals in the catalytic oxidation of aldehydes is interaction of an oxidised form of a metal ion with a hydroperoxide. This reaction probably cannot be regarded as the elementary stage described by Eqn. (22). It must be remembered in particular that, in the presence of a catalyst, decomposition of the peroxy-acid induced by free radicals is possible. Such induced decomposition has been observed e.g. in the presence of cobalt and iron salts[86].

As shown for the oxidation of hydrocarbons[87], it is assumed that free radicals are generated in the oxidation of aldehydes through formation of an intermediate complex between the catalyst and an aldehyde or a peroxy-acid molecule. Kinetic evidence of the formation of complexes with the catalyst has been obtained for perbenzoic acid[83], benzaldehyde[37], peroxypropionic acid[75], and peroxyacrylic acid[57]. It was shown[57] by spectroscopic methods that, when complex compounds are used to catalyse the oxidation of acrylaldehyde, an aldehyde molecule takes the place of one of the ligands, being coordinated through its carbonyl group with the central atom of the catalyst. The same views on the entry of an aldehyde molecule in hydrated form into the coordination sphere of the Co^{3+} ion have appeared[88] in a study of the oxidation of pyridinecarbaldehyde in aqueous medium. An oxygen molecule may enter the intermediate catalytic complex[89,90]. On the whole, however, the question of the existence and the role of catalytic complexes in chain initiation has been developed in considerably less detail than for the oxidation of hydrocarbons, where the decisive role of such complexes in the breakdown of hydroperoxides has been proved unambiguously by both kinetic and physical methods[91,92].

In the presence of a catalyst chains can be initiated not only by reactions (20)–(22) but also by detachment of hydrogen from the alkyl group[34,93]:

$$RCH_2CHO + Mn^{3+} \rightarrow R\dot{C}HCHO + Mn^{2+} + H^+. \qquad (23)$$

Acyl radicals are then formed by a secondary reaction:

$$R\dot{C}HCHO + RCH_2CHO \rightarrow RCH_2CHO + RCH_2CO^{\cdot} \qquad (24)$$

This mechanism of initiation was supported by the isotope effect $k_H/k_D = 5.5$–6.0 obtained for α-deuterated acetaldehydes, whereas no isotope effect was present when the carbonyl hydrogen was replaced by deuterium. Additional evidence for reaction (23) is the detection in the mixture, on addition of an alkene, of products formed by addition of $\cdot CHR.CHO$ radicals to the double bond of the alkene[93].

In the homogeneous catalysis of the oxidation of aldehydes, as in the uncatalysed ocidation, chain-initiating reactions may involve either the free peroxy-acid or its addition product with the aldehyde (an "adduct"). The relative concentrations of adduct and free-peroxy acid, and hence their contributions to the generation of free radicals, depend mainly on the temperature and the aldehyde concentration. Cobalt salts accelerate decomposition of the adduct at temperatures above 10°C. A molecular reaction has been postulated[94] leading to oxidation of the cobalt by interaction between the catalyst and the adduct:

$$CH_3C(O)OOCH(OH)CH_3 + 2Co(OOCCH_3)_2 + CH_3COOH \rightarrow 2Co(OOCCH_3)_3 + CH_3CHO + H_2O.$$

Another postulate[95,96] is radical decomposition of the adduct:

$$Co^{2+} + CH_3CH(OH)-OO-C(O)CH_3 \rightarrow Co^{3+} + CH_3CH(\dot{O})OH + CH_3COO^- \ .$$

These reactions become more important at high aldehyde concentrations, when the equilibrium between the peroxy-acid and the adduct is displaced towards formation of the latter. With decrease in the aldehyde concentration reaction (20) becomes the main process converting the metal ion to a higher valency state. The oxidised form of the metal is obviously able to interact not only with the peroxy-acid but also with the adduct to form free radicals.

Decomposition of Peroxy-acids

In the presence of a catalyst a peroxy-acid may undergo decomposition not only by reactions (20) and (22) but also by homolysis of the oxygen–oxygen bond, as has been proved[57,97,98] by the formation of carbon dioxide (resulting from decarboxylation of $RCOO\cdot$ radicals—products of the cleavage of peroxyacrylic and peroxytoluic acids at the peroxy-bond).

In the presence of catalysts peroxy-acids undergo not only radical but also molecular decomposition with formation of the corresponding carboxylic acids. Molecular breakdown has been established for peroxyacrylic[57], peroxypropionic[57], and peroxybutyric[90] acids. It is significant that this process is observed mainly when carboxylic acids are used as solvents. In the presence of a heterogeneous catalyst—silver oxide—decomposition of peracetic acid in the presence of acetic acid takes place by a molecular mechanism at temperatures of 20–40°C.[26] When the temperature is raised to 70°C, a small proportion of the peroxy-acid breaks down into radicals at the oxygen–oxygen bond. The rate of decomposition of the peroxy-acid diminishes with increase in the concentration of silver oxide.

Chain Propagation

In both catalysed and uncatalysed oxidation the chain-propagating reaction leads to formation of a peroxy-acid as primary molecular product. Involvement of the catalyst in propagation has been shown in the oxidation of hydrocarbons[99], but direct experimental evidence has not been obtained for aldehydes. However, the tenfold increase in the ratio $k_2/k_6^{\frac{1}{2}}$ obtained for the oxidation of benzaldehyde in the presence of a manganese salt relative to the uncatalysed process[100] suggests that the catalyst does affect the chain-propagating reaction. The heterogeneous catalyst Ag_2O may take part in propagation in the oxidation of aldehydes in the presence of unsaturated compounds[26].

Little information has been published on the effect of catalysts on the formation of molecular oxidation products. An acyl radical $RCO^{\cdot}$ may form a complex with the catalyst[57], and thus react more readily with oxygen than it decomposes into $R^{\cdot} + CO$. As a consequence, use of a catalyst leads to a decrease in the quantity of carbon monoxide among the reaction products. A decrease in the yield of carbon dioxide in the oxidation of acetaldehyde has been observed in the presence of silver oxide[101]. The probable reason is that radicals attached to a heterogeneous catalyst are unlikely to break down with the formation of carbon dioxide.

The equilibrium constant of adduct formation K_9 is unaffected by the catalyst[58,60]. No data have appeared on the effect of the catalyst on decomposition of the adduct into carboxylic acids ($k_{9'}$). However, it is known that ions of metals of variable valency may take part in the decomposition of carboxylic acids. Thus Mn^{3+}, Co^{3+}, and Ce^{4+} ions react at 50–100°C with carboxylic acids[102–105]:

$$RCOOH + M^{(n+1)+} \rightarrow M^{n+} + \dot{R} + CO_2 + H^+ \ . \qquad (25)$$

Another possible reaction is[106–108]

$$CH_3COOH + M^{(n+1)+} \rightarrow M^{n+} + \dot{C}H_2COOH + H^+. \qquad (26)$$

Intermediate formation of an adduct and its decomposition

$$Co^{3+} + 2C_6H_5COOH \overset{K_{15}}{\rightleftarrows} [Co^{3+} \cdots 2C_6H_5COOOH] \xrightarrow{k_{15}} Co^{2+} + C_6H_5COOO^{\cdot} + C_6H_5COOH + H^+ \qquad (27)$$

have been discussed[37]. A peculiar feature of the action of salts of metals of variable valency in oxidising processes is the dual function of the catalyst—accelerating at low concentrations of the metal salt in the reaction mixture, and inhibiting at high concentrations.

Chain Termination

Since it was first shown that the catalyst may be involved in the termination of chains[109,110], there are indications that this occurs also in the oxidation of aldehydes. Thus the oxidation of benzaldehyde[84] in the presence of a sufficiently high concentration (~10^{-3} M) of cobalt(II) acetate as catalyst has an induction period directly proportional to the catalyst concentration and inversely proportional to the initial aldehyde concentration. Completion of the induction period coincides with complete conversion of cobalt(II) into cobalt(III). This was explained by the presence of an unpaired electron in cobalt(II) compounds, which (at high concentrations) play a considerable part in the destruction of radicals, whereas cobalt(III) contains no unpaired electrons and does not interact with free radicals.

Chains may be terminated by interaction of the benzoylperoxy-radical $C_6H_5COOO^\cdot$ with cobalt(II) acetate or its dimer. However, data given[84] on the inhibiting action of ions of other metals are fairly contradictory and require further refinement. It was stated[84] in particular that copper(II) even in high concentrations does not bring about an induction period in the oxidation of benzaldehyde. Yet copper(II) at concentrations of ~0.05 M strongly inhibits the oxidation of hydrocarbons[110].

Experimental results on the oxidation of *p*-tolualdehyde in the presence of cobalt salts[85] are reported on the hypothesis that chain termination takes place on acyl radicals $RCO^\cdot$. Similarly[54] chain termination by reaction (10) with the formation of butane-2,3-dione has been established in the oxidation of acetaldehyde catalysed by cobalt acetate. The formation of considerable quantities of this dione (up to 10% on the acetic acid formed) may indicate that the catalyst accelerates recombination of acyl radicals, making it competitive with the chain-propagating reaction (5). Nevertheless, reaction (10) does not strictly involve termination, since the butanedione formed can itself undergo further oxidation by a radical–chain mechanism[112]. The ratio of the rate of accumulation of carbon dioxide to that of acetic acid in the oxidation of butane-2,3-dione is respectively 0.3 and 0.5 in the presence and in the absence of a catalyst[54,112]. This indicates that the catalyst enhances the selectivity of oxidation of the dione to acetic acid.

V. EFFECT OF SOLVENT

Studies of the liquid-phase oxidation of aldehydes have hitherto not included a systematic investigation of the influence of the solvent on the elementary stages. Results obtained in individual researches are qualitative in character and relate mainly to the effect on the overall rate of oxidation.

Current views distinguish two types of solvation—non-specific and specific—of reactant species[113]. Non-specific solvation occurs in all solutions and is due to interaction of the solute with the field of the solvent molecules. One of the main forms of non-specific solvation is caused by electrostatic interaction of reactant species with the medium. The relation between the reaction rate constant k and the dielectric constant of the medium ϵ is expressed by Kirkwood's equation

$$\ln k = \ln k_0 - \frac{1}{kT}\,\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu_A^2}{r_A^3}+\frac{\mu_B^2}{r_B^3}-\frac{\mu_{\neq}^2}{r_{\neq}^3}\right),$$

in which μ is the dipole moment, r is the effective radius of the dipole, and the subscripts A, B, and $\neq$ denote respectively the starting materials and the activated complex. Plots of ln k against $(\epsilon - 1)/(2\epsilon + 1)$ based on published data for the oxidation of aldehydes[26,69,114,115] either are not linear at all or show many points lying outside a linear relation. They suggest that non-specific solvation is not the main factor governing the effect of the solvent on the oxidation of aldehydes.

Specific solvation is due to the formation of various types of complexes between the reactant species and the solvent, e.g. involving hydrogen bonding and π-complexes. The hydrogen bond between a solvent molecule and a peroxy-acid formed by oxidation of an aldehyde may probably either accelerate or retard decomposition of the acid. The selectivity of oxidation of the aldehyde to the peroxy-acid is correspondingly changed.

An increase in the yield of acrylic acid from the oxidation of acrylaldehyde has been observed when water[76], butyric acid, or valeric acid[69] is used as solvent. Water also increases the yield of carboxylic acids from the oxidation of C_2–C_5 saturated aldehydes[116,64]. In the oxidation of isobutyraldehyde water increases the yield of the acid only when present in quantities exceeding 10%; with about 4% of water the yield of the peroxy-acid is increased[64]. In contrast to the above results, acetic acid lowers the yield of peracetic acid obtained by the oxidation of acetaldehyde[26]. Increase in the yield of peroxy-acids in the presence of compounds capable of forming a hydrogen bond has been observed in the oxidation of butyraldehyde in the presence of chloroform and dichloroethane[115], and in the oxidation of acetaldehyde in water and in acetic acid[117].

When benzene, which is able to form π-complexes[118], is used as solvent, carboxylic acids are obtained as the main product of the uncatalysed oxidation of butyraldehyde[115] and benzaldehyde[65]. However, a benzene medium tends to increase the yield of perbenzoic acid from the catalytic oxidation of benzaldehyde[119] and of peracetic acid from that of acetaldehyde[26].

The dependence of the total rate of oxidation of aldehydes on the nature of the solvent can probably be attributed to the effect of the latter not only on the reactivity of the acylperoxy-radicals $RCOOO^\cdot$ in chain propagation but also on chain initiation, as well as on the molecular reactions (16) and (17).

The lower rate of oxidation of acetaldehyde in a carboxylic acid than in acetone can be explained[114] by hydrogen bonding between the acylperoxy-radical and the solvent. The rate of oxidation of benzaldehyde is lower in benzene than in acetone[119], which may be due either to the lower dielectric constant of the solution or to diminished reactivity of peroxy-radicals as a result of "adhering" to the benzene. A similar situation is found[26] for the rate of oxidation of acetaldehyde in various solvents, decreasing in the sequence

$$\text{acetone} > \text{benzene} > \text{acetic acid}\ .$$

The rate of oxidation of acetaldehyde is much lower in cyclohexanone than in other solvents. The solvent effect in this case also may be due to deactivation of peroxy-radicals by hydrogen bonding, since the keto–enol tautomeric equilibrium is displaced considerably further towards the enol with cyclohexanone than with acetone[120]. However, it remains obscure why the decrease in reaction velocity is considerably more marked with cyclohexanone than with other solvents capable of forming hydrogen bonds. The maximum rate of oxidation of acrylaldehyde was found[57] to decrease in the sequence of solvents

carboxylic acids $\geqslant$ aromatic hydrocarbons $>$ aliphatic hydrocarbons $>$ water

The retarding effect of water on the oxidation of aldehydes in the presence of homogeneous catalysts may be due[37] to its ability to form complex hydrates with the catalyst, thereby preventing the latter from taking part in the initiation of chains.

It is quite clear that solvents have a considerable effect on the oxidation of aldehydes, which comprises the aggregate of its effects on the individual stages in the composite process. In order to elucidate the elementrary mechanism of the solvent effect, therefore, separate investigations are required for every elementary stage.

In the oxidation of aromatic and unsaturated aldehydes the solvent may also have a specific influence depending on the structure of the oxidisable substrates. Thus in the later stages of the oxidation of benzaldehyde[66] the effect of the solvent is largely due to its ability to accelerate the formation of autoinhibitors of chain oxidation that may be formed in the oxidation of benzaldehyde, or on the other hand to prevent their formation. In the oxidation of acrylaldehyde[57] the solvent effect is largely governed by the influence on polymerisation of the initial aldehyde and of the resulting acid. Rates of radical polymerisation are considerably higher in non-polar than in polar media. The resulting polymer is able to deactivate the catalyst, with a consequent decrease in the rate of the process.

VI. USE OF THE OXIDATION OF ALDEHYDES TO OBTAIN CERTAIN OXYGEN-CONTAINING COMPOUNDS

The liquid-phase oxidation of aldehydes forms the basis for the preparation of various oxygen-containing compounds, including processes of industrial value, mainly the oxidation of acetaldehyde. Considerable interest has recently been taken in the liquid-phase oxidation of unsaturated aldehydes—predominantly acrylaldehyde and methacrylaldehyde—and also in the combined (concerted) oxidation of aldehydes and unsaturated compounds as a method for obtaining acids and alkene oxides at the same time.

Preparation of Acids

The liquid-phase oxidation of acetaldehyde is a most important method for the manufacture of acetic acid[121]. The process is usually conducted at about 60°C in the presence of manganese acetate, which is an efficient catalyst also for the preparation of acids by the oxidation of other aldehydes[122,123].

An important problem of chemical technology is to develop an effective method for the direct oxidation of methacrylaldehyde to methacrylic acid in the liquid phase. Large quantities of this acid are required for the production of polyesters, and the existing method of obtaining it from acetone[124] is unable to satisfy the rapidly growing demands of industry.

Several attempts have been made to obtain methacrylic acid from methacrylaldehyde in the presence of homogeneous catalysts, but the results show poor reproducibility and evidently cannot be regarded as reliable. This is indicated also by the fact that manufacture of the acid from the aldehyde has not yet been realised. Thus, when methacrylaldehyde was oxidised with oxygen in benzene medium at 40°C in the presence of copper and nickel acetates as catalysts[125], the selectivity of formation of methacrylic acid was 99% with 60% conversion of the aldehyde. The yield of the acid did not exceed 40%, and a large quantity of polymeric products was formed. However, these results could not be repeated by workers[126] who proposed to obtain methacrylic acid by oxidising the aldehyde in alkaline medium in the presence of silver oxide. Nevertheless, despite the great selectivity of formation of the acid, this process, requiring the use of alkaline solutions, can hardly find industrial application. Conducting the oxidation in the presence of such catalysts as cobalt and manganese acetates and acetylacetonates, as well as vanadium compounds, gave the best results[127] with cobalt acetate (the same catalyst as before[125]), when the yield of methacrylic acid reached 80%.

The above results show that, with the exception of the classic catalyst of liquid-phase oxidation—cobalt acetate—sufficiently effective specific catalysts for the oxidation of methacrylaldehyde are not yet available. A promising approach to the problem is thus to develop new catalytic systems based on heterogeneous catalysts, which possess high selectivity and, in contrast to homogeneous catalysts, do not result in contamination of the product with metal compounds.

VII. CONCERTED OXIDATION OF ALDEHYDES WITH OTHER ORGANIC COMPOUNDS

Concerted oxidation provides a highly effective method for obtaining valuable oxygen-containing products, one of which is the carboxylic acid corresponding to the initial aldehyde. The available oxygen of the acylperoxy-radicals and the intermediate products (peroxy-acids) is used to oxidise the second component of the pair. This method was suggested in 1962[2,128,129], when methyloxiran and acetic acid were obtained simultaneously by the concerted oxidation of propene and acetaldehyde. The efficiency of the process has since been improved considerably[101,130] by the use of heterogeneous catalysts, in particular silver oxide. The process is conducted in air compressed to 30-50 atm at 60-100°C.

In the catalytic process the required products are rapidly obtained in high yields—1300 kg of acetic acid and 800 kg of methyloxiran per tonne of acetaldehyde that has reacted—respectively 97 and 60 mole %. The catalytic action of the silver oxide can be explained by involvement of the heterogeneous catalyst in chain propagation[26]:

$$[\mathrm{CH_3COOO} \cdots \mathrm{Ag_2O}]^{\cdot} + \mathrm{C_3H_6} \rightarrow \mathrm{C_3H_6O} + \mathrm{CH_3COO^{\cdot}} + \mathrm{Ag_2O} \ .$$

Concerted oxidation with aldehydes can be used for the epoxidation not only of propene but also of other unsaturated compounds, e.g. allyl chloride[131,132], as well as for introducing oxygen into other classes of organic compounds, including saturated compounds. Thus amines of the piperidine series can be converted by concerted oxidation with benzaldehyde into the corresponding stable iminoxyl radicals[26].

Acetic Anhydride

An important industrial product of the oxidation of acetaldehyde is acetic anhydride[43,96], for which the best catalyst is a mixture of copper and cobalt acetates. The reason is that Co^{3+} and Cu^{2+} ions react readily with an acyl radical:

$$\mathrm{CH_3CO} + \mathrm{Cu^{2+}} \rightarrow \mathrm{CH_3\overset{+}{C}O} + \mathrm{Cu^{+}} \ .$$

This competes with reaction (5) (addition of oxygen to the acyl radical) and ultimately results in formation of an anhydride:

$$CH_3\overset{+}{C}O + CH_3COOH \rightarrow CH_3C(O)O{-}C(O)CH_3 + H^+ \ . \qquad (28)$$

The chief difficulty in the industrial production of acetic anhydride is its ready hydrolysis. This is prevented by the use of high concentrations of the catalyst, which permit short times of contact and relatively low temperatures (~40°C).

Preparation of Peroxy-acids

Peroxy-acids are formed in the act of chain propagation in the oxidation of aldehydes. In order to diminish their reactivity in subsequent transformations and increase their concentration in the mixture the oxidation is conducted at comparatively low temperatures (0–30°C). Furthermore, many publications, mainly patents, give a selection of solvents and catalysts. Data on the effect of the former is fairly contradictory, and it can be stated with some certainty only that ethyl acetate and benzene are among the best solvents for this purpose. Very many catalysts have been proposed. Thus, in order to obtain peracetic acid, the use has been suggested of cobalt(II) nitrate[133] and acetate[114], a mixture of iron monophenoxide and 2,4,6-trinitroresorcinol, a mixture of the latter and cobalt naphthenate, a mixture of cobalt(II) and iron(III) nitrates with concentrated hydrochloric acid, a mixture of cobalt and iron salts of dicarboxylic acids having pK_a = 4.6, and also additions of 60% nitric acid[134]. Manganese compounds—e.g. manganese salts in the presence of water[117] or manganese naphthenate mixed with selenium dioxide—are used as catalysts. The oxidation of acetaldehyde catalysed by iron citrate and naphthenate yields peracetic acid with nearly 100% selectivity. When malonic acid is used as catalyst, the oxidation of acetaldehyde (at 25–30°C) gives a mixture of peracetic acid and its adduct with the aldehyde, in relative amounts depending on the catalyst concentration. Use of the heterogeneous catalyst Ag_2O produces a considerably higher yield of peracetic acid than obtained in the uncatalysed process[101]. Photochemical initiation is also used to increase the concentration of peroxy-acids.

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Prebiological Synthesis of Aminoacids and the Search for them in Meteorites and Lunar Rocks

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New data on various prebiological syntheses of aminoacids and the detection of very small amounts of aminoacids in meteorites and lunar rocks are reviewed. Data are presented concerning the possible precursors of these aminoacids. The hitherto obscure problem of the mechanisms of the formation of aminoacids under the conditions of prebiological synthesis is considered.

The bibliography includes 156 references.

CONTENTS

I. INTRODUCTION

By 1974 fifty years had elapsed since Academician A. I. Oparin's theory of the origin of life was proposed[1]. The Soviet biochemist was the first to formulate a hypothesis concerning the nature of the primary atmosphere on Earth and the possibility of forming complex compounds such as proteins and nucleic acids from the elements as a result of chemical and physicochemical processes in the atmosphere and in the ocean. These processes would have occurred spontaneously under the influence of ultraviolet radiation from the sun, the energy of electric discharges, volcanic heat, and the ionising radiation from terrestrial radioactive rocks. Oparin's idea, subsequently supported by Haldane[2], received the first experimental confirmation after 30 years as a result of the studies carried out by Miller, who succeeded in simulating the formation of biologically important molecules in a non-living system imitating Earth's primitive atmosphere[3,4].

Sciences such as organic and bio-organic chemistry, biochemistry, cosmochemistry, astrophysics, selenology, and others have played an appreciable role in the elaboration and development of the theory of the origin of life. The fundamental studies in this field are being prosecuted in two directions. The first direction, involving synthetic research, was initiated about 20 years ago. Theoretical and experimental investigations led to the accumulation of an enormous amount of data on the synthesis of aminoacids, polypeptides, purine and pyrimidine bases, porphyrins, and monosaccharides under the conditions of the primitive planet as reproduced in the laboratory[5-9]. The development of this research was stimulated afresh by recent radioastronomical observations, which indicate the presence in interstellar matter of molecules important for chemical evolution, such as those of ammonia, water, hydrogen cyanide, cyanoacetylene, acetaldehyde, and others[10].

The second direction involves analytical research. Here studies in the last 5-7 years have been concentrated on the analysis of the carbonaceous material in meteorites and lunar rocks, as well as interstellar matter. Exceptionally important results have been obtained in this field, which permit an answer to the questions whether or not organic compounds of extraterrestrial origin exist, what is their composition, and how they have been formed.

Both prebiological synthesis and analysis of aminoacids are considered in the present review. Recently, all the protein and a number of non-protein aminoacids have been successfully synthesised by non-biological methods or have been detected in objects of extraterrestrial origin (lunar rocks, meteorites), but the mechanisms of formation of these aminoacids have still been little studied.

II. AMINOACID PRECURSORS. THE SEARCH FOR AMINOACIDS IN METEORITES AND LUNAR ROCKS

Cosmic Space

The initial elements required for the synthesis of organic compounds (H, C, O, and N) are formed on a cosmic scale in the central regions of stars at very high temperatures. Diffusional and convective processes displace them towards the surfaces of stars. In stellar atmospheres at relatively low temperatures diatomic and triatomic species such as C_2, C_3, CH, CH_2, CN, CO, CO_2, NH, OH, and CH_4 may be synthesised. Astronomical observations have shown that various stellar processes probably lead to the ejection of these and other compounds as well as atoms into the space around the stars and the interstellar space[11]. Among processes of this kind, one may include the explosion of novae and supernovae, stellar pulsations, flares, and winds, and the migration of mass as a result of the pressure difference between the hot surfaces of stars and the cold interstellar space.

Oró[10], who considered the relative abundances of certain chemical compounds and their stability with respect to heat and light, concluded that stable species of the type CO, CN, CH, C_2, C_3, and others, which are ejected into interstellar space, are subsequently hydrogenated and hydroxylated with formation of organic molecules: CH_2O, CH_3OH, HCOOH, HCN, $HCONH_2$, CH_3CHO, HC_2CN, etc.

The following species have been detected by optical measurements in the gaseous components of interstellar clouds and gas nebulae: CH, CN, CH^+, H_2, and CO.[12] Following the development of microwave spectroscopy, it became possible to extend greatly the knowledge of the composition of interstellar matter. Between 1968 and 1970, compounds such as ammonia[13], water[14], formaldehyde[15] (the first organic molecule discovered in interstellar space), and hydrogen cyanide[16] (the second organic molecule found in space) were detected. Turner[17] observed in 1970 an emission spectrum which corresponded to cyanoacetylene. The above five polyatomic molecules discovered in the interstellar space are probably the most important aminoacid precursors; formaldehyde is most widely distributed in space and is frequently called the "cosmic molecule". Together with hydrogen and hydroxy-radicals, it is probably a normal constituent of many regions of the Milky Way[10].

Table 1. Certain chemical compounds detected by radiospectroscopy in cosmic space.

Year of discovery	Compound	Formula of compound	Wave-length, mm	Concn. of cpd.*	References
1968	Ammonia	NH_3	13	$1 \cdot 10^{-7}$	12.13
1968	Water	H_2O	13	—	14
1969	Formaldehyde	CH_2O	62	—	15
1970	Carbon monoxide	CO	2.6	$1 \cdot 10^{-3}$	12.18
1970	Cyanyl radical	CN	2.6	—	19
1970	Hydrogen cyanide	HCN	3.4	$1 \cdot 10^{-7}$	12,16
1970	Cyanoacetylene	$HC{\equiv}C{-}CN$	33	—	17
1970	Methanol	CH_3OH	360	$1 \cdot 10^{-7}$	12.20
1970	Formic acid	HCOOH	180	—	21
1971	Formamide	$CHONH_2$	65	—	22
1971	Methylacetylene	$HC{\equiv}C{-}CH_3$	3.5	—	24
1971	Acetonitrile	CH_3CN	2.7	—	23
1971	Acetaldehyde	CH_3CHO	280	—	10
1971	Thioformaldehyde	CH_2S	95	—	10
1972	Hydrogen sulphide	H_2S	1.7	—	10
1972	Methyleneimine	CH_2NH	56	—	10

*The concentration of hydrogen was adopted as unity.

By the beginning of 1974, 27 cosmic molecules had been discovered (Table 1). The data in Table 1 show that interstellar matter includes all the initial compounds which may serve for the synthesis of biochemically important substances. The problem of the ways in which these initial compounds are synthesised remains open. There exist two hypotheses concerning the formation of interstellar molecules. The first claims that they may be synthesised under the influence of cosmic rays on the surface of dust particles of interstellar nebulae or meteorites from the CO and H_2 adsorbed on them by a mechanism close to that of the familiar Fischer–Tropsch synthesis[25]. The other (ionic) hypothesis presupposes a homogeneous synthesis of complex cosmic molecules as a result of collisions between ions or simple molecules in the gas phase. Thus it is believed that formaldehyde may be formed in space via the following mechanism[12]:

$$H_2^{\bullet} + H_2 \rightarrow H_3^{\bullet} + H;$$

$$H_3^{\bullet} + CO \rightarrow H_3CO^{*};$$

$$H_3CO^{*} \rightarrow H_2CO + H^{*}.$$

According to this mechanism, one may expect the existence in space of HCO^+ ions, which are formed in another decomposition reaction: $H_3CO^* \rightarrow HCO^* + H_2$. Indeed, Buhl and Snyder[26] detected this ion in 1970 at a wavelength of 3.4 mm.

Comets

The primary compounds may have appeared on Earth's surface in different ways. For example, they might have been introduced when the planets of the solar system passed through interstellar clouds and gas nebulae. One cannot rule out the possibility that the organic substances in comets and meteorites may have served as the sources of the simplest aminoacid precursors on Earth. For example, it is believed that the isotopic composition of the carbon in comets is similar to that on Earth[27].

The orbits of certain comets adjoin Earth's orbit and may even intersect it. This suggests the possibility that a certain amount of the material from comets may reach our planet by a direct collision between the comet and Earth or following the incidence on Earth of meteor streams (showers) and other residues from the comet. Comets contain significant amounts of organic compounds. The nucleus of the comet probably includes H_2O, HCN, NH_3, CO, C_2N_2, CH_4, and C_2H_2.[27] The central body of the comet is surrounded by a rarefied atmosphere (an envelope of vaporised molecules), which emits a beam of rays (the tail) in the direction away from the sun. The main component of the gaseous envelope (the "coma") is atomic hydrogen[28]. Other species are also present: H_2, OH, OH^+, O, CN, C_2, C_3, CH_2, CH, CH^+, CO^+, NH, NH_2, etc.[27]; the presence of C_2H radicals is also possible. CO^+, N_2^+, CO_2^+, CH^+, OH^+, and CN have been detected in the comet's tail. These chemical species may arise on photodissociation or ionisation of stable initial molecules. It is also possible that they are formed as a result of chemical reactions occurring on the surface of the nucleus (for example, under the influence of the solar wind).

Meteorites

Meteorites frequently contain the so called carbonaceous material. Carbonaceous chondrites are particularly rich in this material (up to 5 wt.%).[29] It has been established that the carbonaceous material consists of volatile and involatile organic compounds. In this connection, carbonaceous chondrites are of particular interest for the investigation of aminoacid precursors. Data on the nature of the organic compounds in meteorites have been fully reviewed by Vdovykin, who surveyed scientific data which have accumulated on this problem since 1806.[30] Studies in recent years have shown that meteorites contain not only aminoacid precursors (for example, alkanes ranging from C_1 to C_{26})[30,31] but also aminoacids themselves.

Aminoacids were found previously in many carbonaceous chondrites, but until 1970 the majority of investigators held the view that these aminoacids are probably of terrestrial biological origin and that they are present in the material of the meteorite as a result of contamination[32]. The aminoacid composition of the mixture closely resembled that of human fingerprints. Furthermore, it was shown that aminoacids detected in two meteorites had mainly the L-configuration[33].

Indeed, the problem of biological contamination continues to arise at various stages of experiments on specimens of extraterrestrial origin. Biological impurities can completely distort the true qualitative and quantitative composition of the aminoacid mixture[32,34]. If criteria were available for distinguishing between molecules of biological and non-biological origin, it would be possible to detect reliably biological impurities in the aminoacid mixtures analysed. The general approach to the solution of this problem is based on the differences between the distributions of the enantiomers in the mixtures, between the molecular structures of the individual aminoacids, and between their relative amounts[35,36]. The value of this approach in determining the aminoacid source is somewhat reduced by the racemisation processes[37-41] and the presence in certain micro-organisms (a possible source of contamination) of aminoacids having the D-configuration[42].

The distribution of protein aminoacids in man and bacteria[43] shows that, on contamination by material of human origin, one may expect approximately the following proportions of the four commonest aminoacids, namely glutamic acid : aspartic acid : glycine : leucine = 1.0 : 0.70 : 0.70 : 0.6, while on bacterial contamination we have 1.0 : 0.8 : 0.4 : 0.4.

One should note that aminoacid mixtures obtained in the analysis of contaminations by human fingerprints contain, apart from all the protein aminoacids, also citrulline and ornithine—the metabolic products of the urea cycle[44], which can also be used for the identification of impurities.

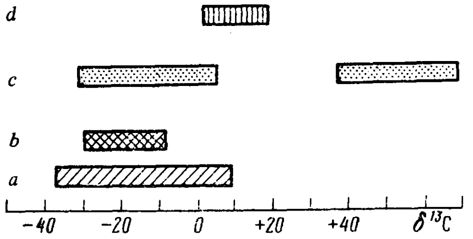

Figure 1. Isotope composition of terrestrial [*a*) total; *b*) biospheric], meteoritic (*c*), and lunar (*d*) carbon.

In the search for aminoacids of extraterrestrial origin, the study of isotopic composition may be of decisive importance. It is known[45] that most of the carbon in Earth's biosphere has an isotope composition† ranging from −29 to −8‰ [of carbon-13] (Fig. 1). The content of the heavy isotope in meteoritic carbon reaches up to +70‰.[46] Such an isotope ratio does not obtain in any of the known sources of carbon on Earth. Consequently these data might indicate indirectly the extraterrestrial non-biological origin of the aminoacids in carbonaceous chondrites. The organic substance in meteorites is also greatly enriched in deuterium[29].

The recent fall of the Murchison meteorite (in 1969) made it possible to obtain specimens with minimal biological contaminations. This carbonaceous chondrite contains 2.0 wt.% of carbon and 0.16% of nitrogen[47]. Studies on the Murchison meteorite carried out in three laboratories[47-50] established the presence of aminoacids of non-biological origin. In two investigations[47,48], the meteorite specimen was treated with water and the solution was hydrolysed and separated on an aminoacid analyser. Part of the aminoacid mixture was analysed in the form of 2-butyl-D-esters of *N*-trifluoroacetylaminoacids on a gas–liquid chromatograph combined with a mass-spectrometer[51-54].

The analysis led to the determination of six protein aminoacids with approximately equal proportions of the enantiomers and 12 non-protein aminoacids (Table 2). Gas–liquid chromatography (GLC) showed that nine aminoacids gave rise to separable diastereoisomeric derivatives (Fig. 2). They all probably exist in the form of racemic mixtures. The presence of many non-protein aminoacids in the Murchison meteorite (2-methylalanine and sarcosine, which are very rarely encountered in biological systems), the presence of all the isomers with two and three crabon atoms, and almost all the isomers with four carbon atoms, as well as the high degree of racemisation of the optically active aminoacids indicates a low probability of biological contamination of the meteorite and suggest that non-biological synthesis has been the source of the aminoacids. This conclusion is confirmed by measurements of the isotope ratio $^{13}C/^{12}C$, which show that the carbon of the Murchison meteorite ($\delta^{13}C$ = +4.4 − +5.9‰) differs appreciably from the carbon of Earth's biosphere (between −8 and −29‰).

The maximum concentrations of the protein aminoacids of the Murchison meteorite were those of glycine (6 μg g^{-1}), alanine (3 μg g^{-1}), glutamic acid (3 μg g^{-1}), valine (2 μg g^{-1}), and proline (1 μg g^{-1}). A similar distribution of aminoacids in this meteorite was found by another group of investigators[49], who analysed it by a highly sensitive and rapid ion-exchange chromatographic method. They also analysed the Murray and Allende carbonaceous meteorites, the results for the former being analogous to those for the Murchison meteorite, while in the latter no aminoacids were detected (the specimens contained only 0.007% of nitrogen).

The total amounts of 10 aminoacids in the Murchison and Murray meteorites were 22 and 21.5 μg g^{-1} respectively[49]. The amount of each of the 8 aminoacids of the non-protein type was smaller than that of the protein aminoacids, with the exception of α-aminoisobutyric acid, the concentration of which was at the level of those of the protein aminoacids. A more detailed analysis of the Murray meteorite[55], carried out by the method used in the studies of Kvenvolden and coworkers[47,48], established that this meteorite contains at least 18 aminoacids. The ratios of the D- and L-isomers of some of them are analogous to the ratios in the Murchison meteorite (Fig. 2). It has recently been established by the same analytical techniques[56] that one of the oldest carbonaceous chondrites (the Orgueil chondrite which fell in France in 1864) also contains aminoacids, some of which are probably of non-biological origin, since they are present in the form of racemic mixtures (Table 2).

The Moon

The analyses of lunar rocks supplied by Soviet and American spaceships are of undoubted interest. The search for aminoacid precursors in these rocks revealed the presence of hydrocarbons, carbides, and other compounds. For example, the experiments of Abell et al.[57], who treated lunar dust with deuterated acids (a 38% solution of DCl in D_2O and a 20% solution of DF in D_2O), led to the discovery of methane and ethane as well as carbides. The specimens of lunar rocks brought by the Apollo 11 and 12 expeditions evolved hydrocarbons on treatment with hydrofluoric, orthophosphoric, or sulphuric acid, one of the main components of which was methane[58,59]. Grinding the lunar rocks in glass ball mills also resulted in the evolution of methane which was probably present in a free state as inclusions (gas bubbles) in the solid rock.

Lunar rocks obtained by the recent Apollo 16 and 17 expeditions contained approximately the same amount of

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† The isotope composition of carbon ($\delta^{13}C$) is quoted in parts per thousand (‰) relative to the composition of the carbonaceous material of the fossil belemnite adopted as the standard.

Table 2. Aminoacids obtained in non-biological syntheses and detected in meteorites and lunar rocks (the molar composition is given; for the lunar specimens, in 1×10^{-9} mole per gramme of rock).

No.	Aminoacid	Non-biological syntheses									Analysis of extraterrestrial specimens						
		in electric discharges				on u.v. irradiation	thermal				meteorites***				lunar rocks from Apollo expeditions		
		1*	2	3	4	5	6	7	8**	9	10	11	12	13	14	15	16
1	Alanine	27.4	+	+	+	+	16.9	20.2	10.0	5.0	+	+*D*, *L*	+*D*, *L*	+*D*, *L*	19	3	7
2	Arginine	—	—	—	—	+	—	—	1.2	—	+	—	—	—	—	—	—
3	Aspartic acid	0.3	+	+	+	—	2.5	15.2	12.5	1.3	+	+*D*, *L*	+*D*, *L*	+*D*, *L*	5	2	7
4	Valine	—	—	—	+	+	1.2	2.1	3.5	0.4	+	+*L*	+*D*, *L*	+*D*, *L*	<1	<1	—
5	Histidine	—	—	—	—	—	—	—	2.0	—	+						
6	Glycine	50.8	+	+	+	+	68.8	24.4	16.8	39.5	+	+	+	+	52	70	57
7	Glutamic acid	0.5	+	+	+	+	3.1	10.2	27.0	1.6	+		+*D*, *L*	+*D*, *L*	11	6	13
8	Isoleucine	—	+	+	—	+	0.7	2.5	3.7	9.4	+	—	—	—	<1	<1	1
9	Leucine	—	—	+	—	+	1.5	4.6	5.5	0.5	+	—	—	—	<1	<1	3
10	Lysine	—	—	—	—	+	—	—	1.9	—	+	—	—	—	—	—	—
11	Proline	—	—	—	+	—	1.5	2.3	7.4	5.0	+	+*D*, *L*	+*D*, *L*	+*D*, *L*	—	—	—
12	Serine	—	+	+	—	+	1.9	10.0	2.0	4.0	—	—	—	—	10	3	10
13	Tyrosine	—	—	—	—	+	0.4	2.0	0.8	—	+	—	—	—	—	2	—
14	Threonine	—	+	+	—	+	0.6	3.0	2.3	—	—	—	—	—	3	—	2
15	Phenylalanine	—	+	—	—	—	0.6	2.2	2.1	1.2	—	—	—	—	—	—	—
16	Isoserine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
17	α-Aminoisobutyric acid	—	+	—	—	—	—	—	—	—	+	+	+	+	—	—	—
18	α-Amino-n-butyric acid	4.0	—	+	+	—	—	—	—	—	+	—	+*D*, *L*	+*D*, *L*	—	—	—
19	Sarcosine	4.0	—	+	+	—	—	—	—	—	+	+	+	+	—	—	—
20	β-Alanine	12.1	—	+	+	—	+	+	—	—	+	+	+	+	—	—	—
21	β-Aminoisobutyric acid	—	—	—	+	—	—	—	—	—	+	+*D*, *L*	+*D*, *L*	+*D*, *L*	—	—	—
22	β-Amino-n-butyric acid	—	—	—	+	—	—	—	—	—	—	+	+	+	—	—	—
23	γ-Aminobutyric acid	—	—	—	+	—	—	—	—	—	+	+	+	+	—	—	—
24	Isovaline	—	—	—	+	—	—	—	—	—	—	—	+*D*, *L*	+*D*, *L*	—	—	—
25	Norvaline	—	—	—	+	—	—	—	—	—	—	—	+	+	—	—	—
26	*N*-Methyl-β-alanine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
27	*N*-Methylalanine	0.8	—	+	+	—	—	—	—	—	—	—	+	+	—	—	—
28	*N*-Ethyl-β-alanine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
29	αβ-Diaminobutyric acid	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
30	*N*-Ethylglycine	—	—	—	+	—	—	—	—	—	—	—	+	+	—	—	—
31	αβ-Diaminopropionic acid	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
32	γ-Amino-α-hydroxy-butyric acid	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
33	Pipecolinic acid	—	—	—	+	—	—	—	—	—	—	—	+*D*, *L*	+*D*, *L*	—	—	—
34	Norleucine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
35	Alloisoleucine	—	—	—	+	—	0.3	1.4	—	—	—	—	—	—	—	—	—
36	*N*-Propylglycine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
37	*N*-Isopropylglycine	—	—	—	+	—	—	—	—	—	—	—	—	—	—	—	—
38	Ornithine	—	—	—	—	+	—	—	—	—	+	—	—	—	—	—	—

*1) Refs. 3 and 4; 2) Ref. 108; 3) Ref. 105; 4) Refs. 95 and 96; 5) Refs. 102 and 121–123; 6) and 7) Refs. 132 and 133; 8) Ref. 136; 9) Refs. 140 and 141; 10) Ref. 25; 11) Ref. 56; 12) Refs. 49 and 55; 13) Refs. 47 and 48; 14)–16) Ref. 69.

**Methionine was also detected (1.2%).

***+*D*,*L* denotes the presence of enantiomers.

total hydrogen as the specimens brought by the earlier expeditions—between 4 and 206 parts per million[60]. Aminoacid precursors were detected at the level of several parts per 1000 million. Nitrides, carbides, water, carbon dioxide, hydrogen, and various metals and their oxides were found in lunar materials[61]. Hopeful results have now been obtained, suggesting that these materials contain organic products, including aminoacids of non-biological origin. After extraction with cold water in two laboratories of the lunar rocks supplied by the astronauts of the Apollo 11 expedition, aminoacids were not detected[62,63]. All other groups of investigators extracted the specimens with hot water and did discover aminoacids[64-67]. The identification of glycine (32 μg per kg of lunar dust) and alanine (36 μg kg^{-1}) in aqueous non-hydrolysed extracts has been reported[64,67]. Fox and coworkers[65,66] used extraction with hot water followed by hydrolysis. Analysis on an ultrasensitive ion-exchange chromatograph detected glycine and alanine in the same amounts as those obtained by other investigators[64], but threonine, serine, and aspartic and glutamic acids were also found. It has been shown[64,66] that aminoacids are present in lunar rocks mainly as polymers.

A scheme for the complete analysis of organic substances of different classes in lunar materials supplied by the crew of the Apollo 11 spaceship has been described[58,68,69] (Fig. 3). It was developed on the basis of numerous investigations of organic compounds in old rocks and meteorites. In this scheme, organic substances of different classes are extracted in succession from a single large specimen with minimal transfer of materials. Such consecutive tests of lunar specimens did not prove to be

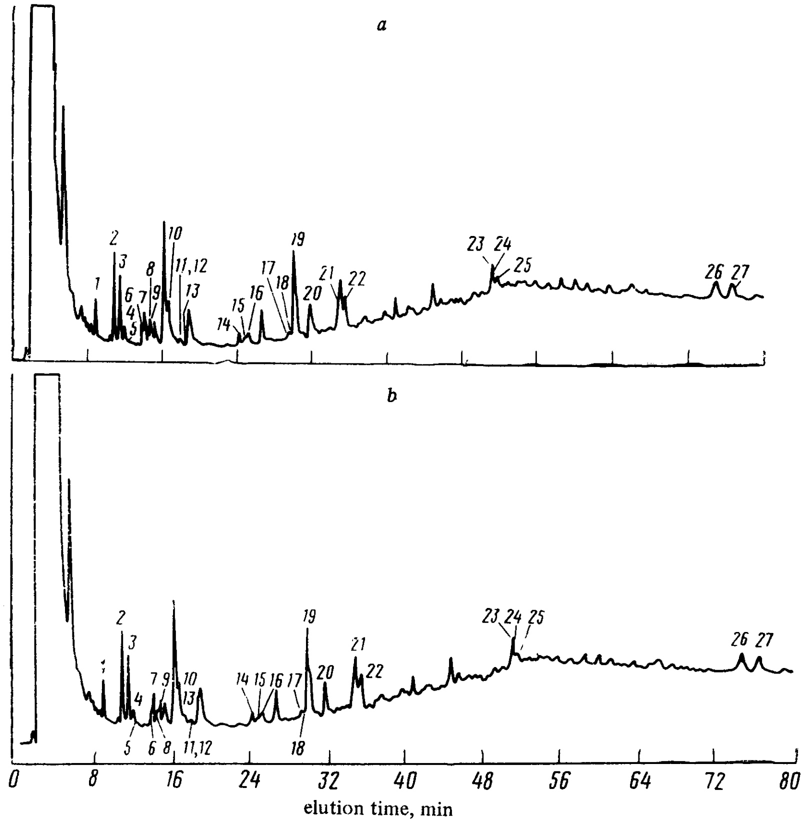


Figure 2. Chromatograms of the aminoacids from the Murchison (*a*) and Murray (*b*) meteorites: 1) isovaline; 2) α-aminoisobutyric acid; 3) D-valine; 4) L-valine; 5) *N*-methylalanine; 6) D-α-aminobutyric acid; 7) D-α-alanine; 8) L-α-aminobutyric acid; 9) L-α-alanine; 10) *N*-methylglycine; 11) *N*-ethylglycine; 12) D-norvaline; 13) L-norvaline; 14) D-β-aminoisobutyric acid; 15) L-β-aminoisobutyric acid; 16) β-aminobutyric acid; 17) D-pipecolinic acid; 18) L-pipecolinic acid; 19) glycine; 20) β-alanine; 21) D-proline; 22) L-proline; 23) γ-aminobutyric acid; 24) D-aspartic acid; 25) L-aspartic acid; 26) D-glutamic acid; 27) L-glutamic acid.

sufficiently effective and were not used in subsequent analyses. However, this unique scheme may be useful in the study of geological and extraterrestrial specimens available in limited amounts.

Yet another scheme has been proposed[70] for the analysis of organic substances in lunar specimens. Here it is suggested that a closed extraction apparatus be used, whereby one can carry out the extraction (with the aid of ultrasound), evaporation, separation on columns with adsorbents, and the collection of fractions in a closed system. Solvents and solutions are transferred from one apparatus to another by the pressure of pure helium. However, the nature of the carbon-containing compounds in lunar rock precluded the application of this scheme. Nevertheless, there is hope that this idea may prove useful in designing an apparatus for the remote investigation of the organic substances present on other planets.

The techniques used in the extraction and hydrolysis of the lunar specimens supplied by the Apollo 11 and 12 expeditions have been described in detail also in other reports[71-73], which likewise confirm that schemes in which provision is made for the isolation of any one class of compounds are the most rational.

Thus in the analysis of the first lunar specimens use was made of three methods involving extraction by aqueous and non-aqueous solvents: boiling in open and closed systems, Soxhlet extraction, and extraction with the aid of ultrasound[59]. It has been shown that aminoacids and their precursors may be most effectively sought by extraction with hot water followed by acid hydrolysis of the aqueous extract[65]. Extraction with non-aqueous solvents and direct acid hydrolysis of the lunar specimens do not yield positive results[59,62,63]. Direct hydrolysis of the lunar specimen with 6 *N* HCl is accompanied by the formation of a very large amount of salts, which greatly impair the extraction process. It may be that treatment of lunar rocks with hot hydrochloric acid leads to the decomposition of aminoacids[59,74]. Extraction with water

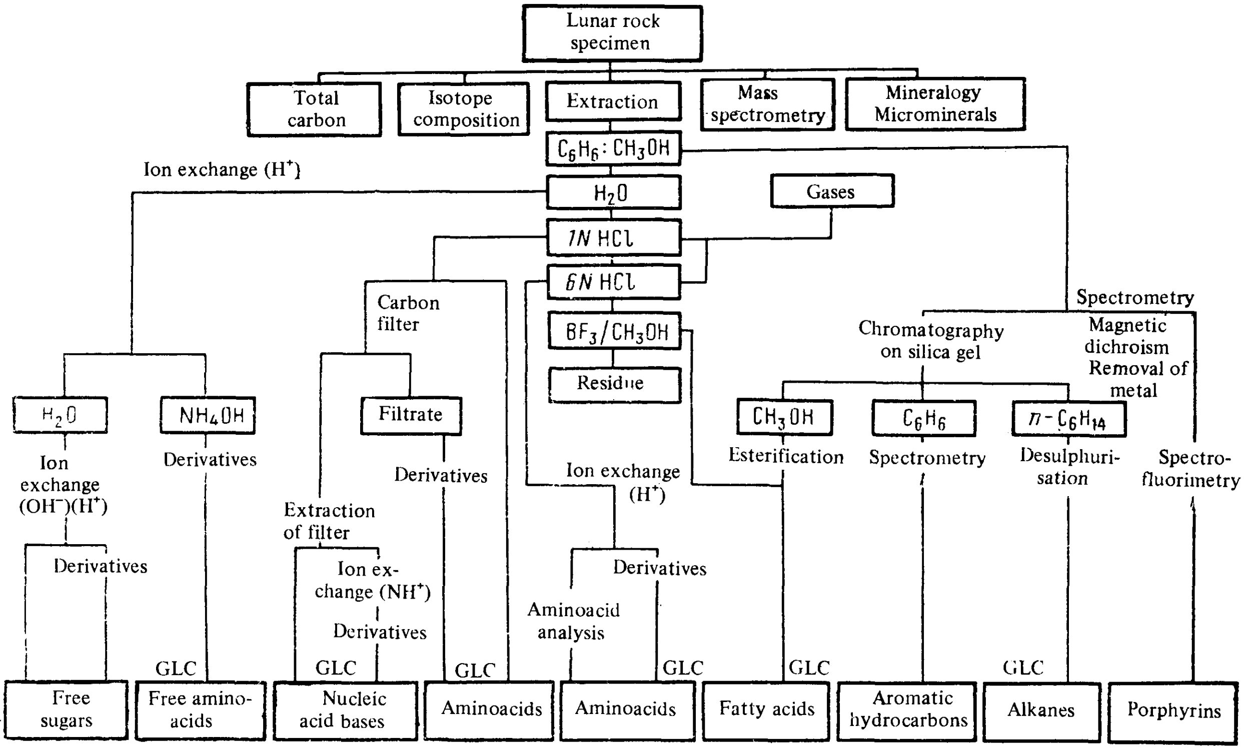


Figure 3. A scheme for the complete analysis of organic compounds in lunar rocks[65].

followed by the hydrolysis of the extract (indirect hydrolytic scheme) has been rapidly adopted and used to search for aminoacids in other specimens of lunar rocks and in meteorites.

Together with a detailed description of the analytical technique for lunar rocks provided by the Apollo 11, 12, and 14 expeditions, the paper by Fox et al.[34] presents also the qualitative and quantitative compositions of the aminoacids detected in such rocks (Table 2). The results in Table 2 show that the same aminoacids were identified in almost all instances.

Analysis of lunar specimens revealed the presence of aminoacids in very small amounts (20–70 parts per 1000 million)[44,65]. It was therefore of interest to test for the presence in these specimens of biological contaminations of terrestrial origin. Comparison of the analytical results for lunar specimens on an ultrasensitive aminoacid analyser with the aminoacid content in fingerprints suggests the absence of such contaminations (Fig.4).[44] A blank experiment demonstrated the absence of aminoacids from the reagents employed.

The possibility that the aminoacids detected might have been formed on oxidation of the rocket fuel (1,1-dimethylhydrazine) on the surface of the Moon was tested directly on a lunar specimen[75]. The specimen was taken from beneath the lunar module of the Apollo 15 expedition after it had been acted upon by the exhaust gases of the engine of the descent apparatus. The results of the analysis of the hydrolysates of this specimen revealed a lower overall amount of aminoacids than in the specimens investigated previously[34,75]. Their qualitative composition proved to be the same. It follows from this that the rocket fuel oxidation products do not contaminate lunar soil with aminoacids. It is possible that the hot exhaust gases actually decompose the lunar aminoacids. Furthermore, oxidation of 1,1-dimethylhydrazine under laboratory conditions does not lead to the synthesis of aminoacids[66].

The study of the isotope composition of lunar carbon also indicates the absence of terrestrial contaminations. The isotope composition of the carbon in lunar rocks, collected in the Sea of Tranquility, varies from +2.2 to +10.8‰ (breccia) and from +15 to +20‰ (lunar powder)[62,76,77]. The distribution of carbon isotopes in the lunar powder specimens supplied by the Apollo 16 expedition varied from +9.4 to +16.1‰ for a total amount of carbon of 88–206 parts per million[61]. Thus, one may assume that lunar carbon is anomalously heavier compared with terrestrial carbon (Fig.1).

The analytical data show that the aminoacids in lunar rocks are present in a bound form and are not terrestrial contaminations or rocket fuel combustion products. The low concentration of aminoacids suggests that they might have appeared on the Moon as a result of the incidence of organic compounds from interstellar matter[78], comets' tails[79], solar wind[60], and meteorites[48]. Interstellar matter probably makes the smallest contribution to the formation of aminoacids on the Moon's surface[80] and solar wind the highest.

The Planets

Data concerning the composition of the atmospheres of the planets in the solar system are very important for the determination of aminoacid precursors (Table 3). Table 3 shows that Earth differs strongly from the other planets in the composition of the atmosphere, which is probably due to the presence of life on Earth. The exact composition of the primary terrestrial atmosphere is unknown. Oparin assumed that Earth was formed by a cold process and its atmosphere might therefore have contained hydrogen, methane, and the inert gases[1]. This reducing atmosphere was gradually enriched in the gases evolved from the Earth's core—methane, hydrogen sulphide, and ammonia. It probably also contained water vapour. An atmosphere having this composition might have served as a source of various organic substances on Earth. Numerous subsequent experiments confirmed the possibility of the synthesis of aminoacids under the reducing conditions of the primary terrestrial atmosphere. Experiments simulating Jupiter's atmosphere[82] also demonstrated the possibility of the synthesis of organic compounds which are precursors of biologically important molecules.

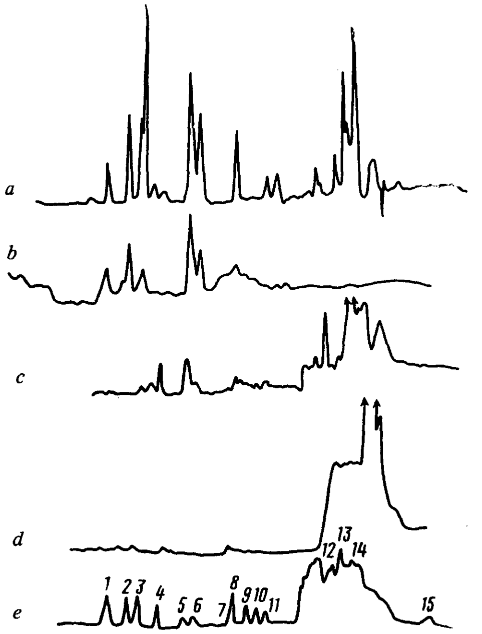


Figure 4. Chromatograms of aminoacid mixtures obtained in separation on an ion-exchange analyser[44]: *a*) contaminations by human fingerprints; *b*) hydrolysate of the aqueous extract of lunar dust (Apollo 11); ditto (Apollo 12); *d*) aqueous solutions in a blank experiment; *e*) mixture of standard aminoacids [1) aspartic acid; 2) threonine; 3) serine; 4) glutamic acid; 5) glycine; 6) alanine; 7) cysteine; 8) valine; 9) methionine; 10) isoleucine; 11) leucine; 12) histidine; 13) lysine; 14) ammonia; 15) arginine].

Some investigators believe that the atmosphere of the primitive Earth was not entirely reducing[83]. The primitive atmosphere might have been formed from the gases evolved from the Earth's mantle and core. Methane, carbon dioxide, and a number of radicals (C_2, C_3, CH_3, CN, etc.) are formed at present in the Earth's mantle and were probably formed during the cooling of the fused Earth[84,85]. The primary atmosphere might have been close in composition to that of volcanic gases. The gases which are ejected by volcanoes at the present time contain largely CO_2, CO, CH_4, H_2, N_2, and possibly HCN.[86-88] In 1973 Soviet investigators succeeded in confirming that volcanic gases contain hydrogen cyanide—a most important aminoacid precursor[89]. Its concentration in the gases evolved by the incandescent lava (at 900°C) of the volcano Alaid in the Kuril islands is about 0.01 mg $litre^{-1}$. Aminoacids and their precursors have been obtained from gases having a composition close to that of volcanic gases (see the next Section). The data presented show that, during certain periods of evolution, the atmosphere of the primitive Earth might have had a composition resembling that of the atmospheres of Jupiter and Saturn (the "fossil" planets) or Venus and Mars.

Table 3. The compositions of the atmospheres of the planets in the solar system[13,81] (the components are listed in order of decreasing concentrations).

Planet	Components
Venus	CO_2,CO, HCl, HF, H_2O (O_3?), (N_2?)
Earth	N_2, O_2, H_2O, Ar, CO_2, Ne, He, CH_4, Kr, N_2O, H_2, O, O_3, Xe
Mars	CO_2, CO, H_2O, O_2, (CH_4?), (NH_3?), (N_2?)
Jupiter	H_2, CH_4, NH_3
Saturn	H_2, CH_4, (NH_3?)
Uranus	H_2, CH_4
Neptune	H_2, CH_4

When an oxidising atmosphere is simulated (a mixture of CO_2, H_2O, N_2, and O_2), it is impossible to synthesise important aminoacid precursors such as HCN, CH_3CHO, CH_3NH_2, etc.[90] Thermodynamic calculations have shown that, under the conditions of a reducing atmosphere (a mixture of NH_3, H_2, H_2O, and CH_4), the enthalpies of formation of these compounds are an order of magnitude lower than in an oxidising atmosphere.

The principal ways in which the most important aminoacid precursors (methane, hydrogen cyanide, cyanoacetylene, the simplest aldehydes, and others) are synthesised have been thoroughly examined[5,8,9]. For example, it is known that hydrocarbons may be formed at an elevated temperature from carbon and hydrogen, a mixture of carbon monoxide or dioxide with hydrogen, and also when metal carbides are acted upon by water. Hydrogen cyanide is obtained in electric discharges between carbon electrodes in an atmosphere of nitrogen and hydrogen, nitrogen and methane, or carbon monoxide and hydrogen. Under the same conditions, cyanoacetylene may be formed. Lower aldehydes may be synthesised by the action of ultraviolet radiation or an electric discharge on CO_2-H_2O, $CO-H_2O$, CH_4-H_2O, and even $CO-H_2$ mixtures.

Thus the most varied primary compounds, which are of interest as aminoacid precursors, might have existed in the atmosphere or hydrosphere of the primitive Earth. To some extent, they might have been brought to Earth from space in one way or another or they might have arisen spontaneously from the simplest organic and inorganic substances present on Earth itself. During chemical evolution, these compounds, particularly methane, ammonia, water, formaldehyde, and hydrogen cyanide, served as the starting materials in the non-biological syntheses of various biologically important substances, particularly aminoacids.

III. PREBIOLOGICAL SYNTHESIS OF AMINOACIDS

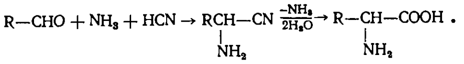
The majority of the syntheses of aminoacids require the expenditure of energy. Under the conditions of the primitive Earth, the following different energy sources might have existed: ultraviolet radiation from the Sun—570.0 cal cm^{-2} per year ($\lambda < 250$ nm); electric discharges (atmospheric lightning)—3.9 cal cm^{-2} per year; radioactive emission from the Earth's core (at depths down to 1 kilometer)—0.8 cal cm^{-2} per year; volcanic heat (as a result of magmatic activity)—0.13 cal cm^{-2} per year; cosmic rays—0.0015 cal cm^{-2} per year [91].

a. Synthesis in Electric Discharges

Aminoacids were obtained for the first time under laboratory conditions by Miller [3,4,92] when a mixture of gases simulating the atmosphere of the primitive Earth were subjected to the action of electric discharges. Miller's apparatus consisted of a 5-litre flask (fitted with two electrodes), through which a mixture of water vapour, methane, ammonia, and hydrogen circulated. A potential of 60 kV was applied to the electrodes and the arc was struck.

After incubation for a week, it was found that HCN, HCHO, CH_3CHO, aminoacids, hydroxyacids, carboxylic acids (Table 2) urea, and *N*-methylurea had been synthesised. Altogether 11 aminoacids were found, glycine, α-alanine, β-alanine, and α-aminobutyric acids being obtained in amounts sufficient for identification on the basis of the melting points of their derivatives.

Miller [34,92] suggested two possible pathways to the synthesis of aminoacids: (1) their generation in the gas phase from the radicals and ions formed in the electric discharges from mixtures of methane, ammonia, and water; (2) the formation in the gas phase of only the simplest aldehydes and nitriles, which are then converted into aminoacids in the liquid phase. The secondary pathway appears to be more likely. Analysis of the gas phase reveals the presence of HCN, HCHO, and CH_3CHO, their amount increasing to a maximum at the beginning of the reaction and then falling. These observations enabled Miller to suggest the occurrence of the Strecker reaction in the synthesis of aminoacids and hydroxyacids in the liquid phase. Aminonitriles should have been formed as intermediates:



$$R{-}CHO + NH_3 + HCN \rightarrow \underset{\displaystyle NH_2}{RCH}{-}CN \xrightarrow[2H_2O]{-NH_3} R{-}\underset{\displaystyle NH_2}{CH}{-}COOH\ .$$

To confirm the proposed mechanism, Miller carried out the alkaline hydrolysis of a synthetic mixture of RCHO, HCN, and NH_3. This also yielded glycine, α-alanine, and α-aminobutyric acid. The last two aminoacids were obtained in much greater amounts than in the experiment with an electric discharge. An important confirmation of this mechanism is provided by the detection in the liquid phase of the corresponding hydroxyacids (glycolic, lactic, and α-hydroxybutyric) in approximately equal proportions together with the aminoacids (glycine, α-alanine, and α-aminobutyric acid). This finding suggests that the acids are synthesised simultaneously with equal thermodynamic and kinetic probabilities. The detection of a large amount of formic acid also confirms the importance of the role of hydrocyanic acid as an intermediate in prebiological synthesis.

Some workers believe [86,93,94] that the content of ammonia in the primitive atmosphere of Earth was not more than 10^{-5} atm. This does not, however, diminish the important role which ammonia might have played in the prebiological synthesis of organic compounds in the ocean. In their latest studies Miller and coworkers [95,96] investigated in detail the synthesis of aminoacids in electric discharges in mixtures of methane, nitrogen, and water containing traces of ammonia. They detected 28 aminoacids by ion-exchange chromatography and gas chromatography combined with mass spectrometry (Table 2). Their overall yield was 15.5% (with respect to carbon).

It is noteworthy that previously many investigators found a wide variety of protein and non-protein aminoacids in analogous syntheses. However, the reliable detection in a single experiment of 20–30 aminoacids at once, when these are present in very small amounts, became possible only recently as a result of the great sophistication of analytical techniques.

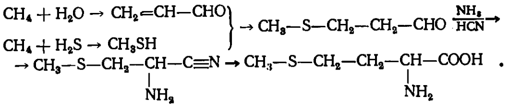
It has been suggested [96] that, when a mixture of methane, nitrogen, and water is subjected to the action of electric discharges, aminoacids are formed mainly via nitriles and aminonitriles. The high content of hydrocyanic acid in the aqueous phase and the fact that the presence of γ-amino-α-hydroxybutyric, $\alpha\gamma$-diaminobutyric, and $\alpha\beta$-diaminopropionic acids and serine is associated with nitrile precursors support this hypothesis. The absence of ammonia from the initial mixture probably rules out the Strecker synthesis in the present instance.

According to Miller, aspartic and glutamic acids are formed by the Strecker reaction via α-cyanoacetaldehyde and β-cyanopropionaldehyde. This is confirmed by the detection in the electric discharges of cyanoacetylene [97], which may be regarded as a precursor of cyanoacetaldehyde.

The mechanism of the synthesis of aspartic acid via diacetylene, which is always present in the gases formed by the electrocracking of hydrocarbons, also appears to be likely [98,99]. At elevated temperatures diacetylene may combine with two ammonia molecules with formation of succinodinitrile. Radical amination of the latter and hydrolysis of the aminodinitrile lead to aspartic acid. Glutamic acid can also be synthesised from diacetylene by the addition of ammonia and water with intermediate formation of β-cyanopropionaldehyde.

By subjecting various hydrocarbons to high temperatures or electric discharges, it is possible to synthesise phenylacetylene [100], which is readily hydrated to phenylacetaldehyde. The yield of the aldehyde increases when the reaction proceeds via the nucleophilic or radical addition of hydrogen sulphide followed by the hydrolysis of the thioaldehyde [101]. Next ammonia and hydrogen cyanide add on by the Strecker reaction with formation of the nitrile of phenylalanine and then of phenylalanine itself. In the radical addition of hydrogen sulphide to phenylacetylene, a low yield of tyrosine was obtained. The above sequence of reactions probably determines the mechanism of the synthesis of these aminoacids in the presence of hydrogen sulphide. However, previously investigators [102,103] detected phenylalanine in mixtures synthesised nonbiologically in the absence of hydrogen sulphide.

The prebiological synthesis of methionine has been achieved [104] by exposing a mixture of methane, nitrogen, ammonia, water, and hydrogen sulphide (or thiomethanol) to an electric discharge. It is believed that acrolein, which has been detected in the resulting mixture, is an intermediate in this reaction:



$$\left.\begin{array}{l} CH_4 + H_2O \rightarrow CH_2{=}CH{-}CHO \\ CH_4 + H_2S \rightarrow CH_3SH \end{array}\right\} \rightarrow CH_3{-}S{-}CH_2{-}CH_2{-}CHO \xrightarrow[HCN]{NH_3}$$

$$\rightarrow CH_3{-}S{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}C{\equiv}N \rightarrow CH_3{-}S{-}CH_2{-}CH_2{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH\ .$$

The authors note that acrolein may be a precursor not only of methionine, but also of homocysteine, glutamic acid, homoserine, and $\alpha\gamma$-diaminobutyric acid. This is possible when hydrogen sulphide, hydrogen cyanide, water, or ammonia add to its double bond.

Experiments[105] analogous to the first experiment carried out by Miller revealed an acceleration of the synthesis of aminoacids. Exposure to electric discharges for the first 20 h led to the formation of two aminoacids, four aminoacids were detected after 100 h, and 12 aminoacids after 200 h. Abelson[106] subjected to the action of electric discharges mixtures of gases with different concentrations of H_2, CH_4, CO_2, CO, H_2O, NH_3, N_2, and O_2. He demonstrated that aminoacids are synthesised only in a reducing atmosphere (oxygen inhibits their formation) and emphasised the role of hydrogen cyanide as an intermediate in these syntheses.

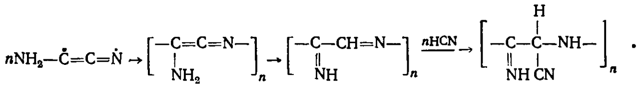
Pavlovskaya and Pasynskii[107] obtained the same set of aminoacids as Miller[3,4] when they exposed to spark discharges a different mixture, which, however, was of a reducing type (CH_4, NH_3, CO, and H_2O). A thermodynamic assessment of the pathway followed in this synthesis showed that aminoacids are formed with a decrease of free energy ($\Delta G_0 = -5.9$ kcal mole^{-1}), while in Miller's model mixtures the free energy increases ($\Delta G_0 = +62$ kcal mole^{-1}), i.e. the conditions are less favourable. The main conclusion reached in this important study involves the hypothesis that the loss of hydrogen from the terrestrial atmosphere could not have been a major obstacle to the synthesis of aminoacids.

Electric discharges have also been used to treat mixtures of methane, ammonia, and water vapour[108]; 45% of the products formed were found in the aqueous phase where the concentration of hydrocyanic acid was highest. After the hydrolysis of the aqueous phase (6 N HCl, 100°C, 24 h), glycine, alanine, aspartic and glutamic acids, threonine, serine, isoleucine, and phenylalanine were found by ion-exchange and gas chromatography. Hydrolysis of the polypeptides, detected in the reaction mixture, yielded the same aminoacids. In the reaction mixture, aminoacids are present in a free state only in trace amounts. It was concluded that, in the presence of a condensing agent (cyanamide), the aminoacids synthesised are converted into polypeptides in the aqueous phase.

Ponnamperuma and Woeller[109], who subjected an anhydrous equimolecular mixture of methane and ammonia to the action of spark discharges (4 kV, 0.5 mA), demonstrated the formation of nitriles and aminonitriles in the gas phase in the absence of aldehydes, which are necessary for Strecker condensations. Only the simplest aminonitriles (aminoacetonitrile and aminopropionitrile) were detected in the reaction gases. After the hydrolysis and esterification of the involatile liquid fraction in an analogous experiment[110], glycine, alanine, sarcosine, β-aminoisobutyric acid, diethylaminomalonic acid, etc. were detected.

These experiments indicate a different mechanism for the formation of aminonitriles—the direct precursors of aminoacids. At the high temperatures of the electric discharge, there is an equilibrium system consisting of molecular acetylene, hydrogen, and many radicals: C_2H, CH, CH_2, CH_3, NH, NH_2, CN, H, etc. When the temperature is reduced, the radicals recombine with formation of molecular compounds: acetylene and its homologues, hydrogen cyanide, cyanoacetylene, nitriles, and aminonitriles. Hydrolysis of the aminonitriles formed in this way yields the corresponding aminoacids.

Having determined the molecular weights of the liquid fractions obtained in similar experiments, Ponnamperuma and coworkers[109-111] concluded that the heavy fractions consist mainly of polymers (M from 2.4×10^2 to 1.4×10^3). The synthesis of these polymers can be accounted for on the basis of polymerisation of hydrogen cyanide[112-114], which is formed in the electric discharges from methane and ammonia. In the gas phase, hydrogen cyanide dimerises spontaneously in the presence of ammonia, forming the aminocyanomethylene biradical $H_2N{-}\dot{C}{=}C{=}\dot{N}$.[115,116] The latter polymerises rapidly and the resulting polymer tautomerises to polyiminoketimine, which interacts with hydrogen cyanide to form polyiminomalononitrile:



$$nNH_2{-}\dot{C}{=}C{=}\dot{N} \rightarrow \left[\begin{array}{c}{-}C{=}C{=}N{-}\\ | \\ NH_2\end{array}\right]_n \rightarrow \left[\begin{array}{c}{-}C{-}CH{=}N{-}\\ \| \\ NH\end{array}\right]_n \xrightarrow{nHCN} \left[\begin{array}{c} H \\ | \\ {-}C{-}C{-}NH{-}\\ \|\quad | \\ NH\ CN\end{array}\right]_n .$$

Hydrolysis of such compounds can lead to the formation of polypeptide chains, which are subsequently decomposed to aminoacids. In this mechanism, hydrogen cyanide is the main precursor of aminoacids, giving rise in an anhydrous gaseous phase to a number of nitriles and imino- and amino-compounds, which are starting materials for the synthesis of aminoacids and polypeptides.

The experiments of Toupance et al.[90] also emphasised the role of the nitrile group in the syntheses of aminoacid precursors from methane–ammonia mixtures in electric discharges (200 V, 100 mA). The infrared spectra (712 cm^{-1}) of the reaction mixture revealed a rapid increase of the concentration of hydrogen cyanide during the first seconds of the experiment. Subsequently its concentration remained unchanged.

Thus the following three pathways to the synthesis of aminoacids are possible under the influence of electric discharges through gases simulating the reducing atmosphere of the primitive Earth: (1) via aldehydes (with subsequent Strecker condensation); (2) via aminonitriles; (3) via nitrogen-containing polymers. It is extremely likely that non-biological synthesis included simultaneously all three mechanisms, particularly since in virtually all of them the principal role is assigned to acetylene and nitrile groups.

b. The Influence of Ultraviolet Radiation

Ultraviolet light has also been used to synthesise aminoacids. Groth and Weyssenhof[117] irradiated for a week with ultraviolet light from a low-pressure mercury lamp (4×10^{18} photons s^{-1}) a mixture of ammonia, methane, and water containing mercury vapour as the sensitiser. However, aminoacids were not detected in the subsequent analysis of the reaction mixture by paper chromatography. In this instance there was probably no direct photolysis of methane in the given wavelength ranges of the radiation and the probability of photosensitisation was low. The radicals and atoms obtained on photolysis or photosensitisation of ammonia (NH_2 + H) are energetically relatively unreactive towards methane at the experimental temperature (50°C). Their reactivity begins to be manifested above 300°C. However, the replacement of CH_4 by C_2H_6 in this experiment led to the formation of aminoacids (the yields are indicated in brackets): glycine (32×10^{-6} M), α-alanine (23×10^{-6} M), and α-aminobutyric acid (0.5×10^{-6} M) as well as carboxylic acids: formic (72×10^{-6} M), acetic (203×10^{-6} M), and propionic (17×10^{-6} M). In the absence of a photosensitiser, the amount of aminoacids synthesised was lower.

When a methane-containing mixture was subjected to the shorter-wavelength radiation of the xenon lamp (147 nm and 129.5 nm, 4×10^{16} photons s^{-1}), aminoacids were also synthesised. In this case very small amounts of glycine and α-alanine were detected. Terenin and coworkers[118,119] achieved the photochemical synthesis of aminoacids from gaseous and liquefied mixtures of methane, ammonia, carbon monoxide, and water. They used a powerful hydrogen lamp whose radiation in the short-wavelength range ($\lambda \geqslant 130$ nm) was closer to the ultraviolet spectrum of the Sun. α-Alanine, α-aminobutyric acid, valine, and norleucine were detected in the synthesis products. Thus, short-wavelength radiation might have been sufficiently effective in the photolysis of mixtures of ammonia, methane, hydrogen, and water. This conclusion was confirmed by their ionisation potentials and quantum yields[120].

The photochemical synthesis of aminoacids from aldehydes and ammonium salts was developed in greatest detail by Pavlovskaya and coworkers[102,121–123]. Aqueous solutions of formaldehyde and ammonium nitrate were irradiated with ultraviolet light at a wavelength of 253.7 nm and 40°C in the course of 20–355 h. The aminoacid fractions, obtained by separation on ion-exchange resins, were analysed by paper and thin-layer (silica gel) chromatography. Serine, glycine, alanine, threonine, and basic aminoacids were detected. The qualitative and quantitative composition of the aminoacids changes somewhat following the irradiation of the initial solutions in the presence of natural adsorbents and catalysts: kaolinite, bentonite, limonite, and quartz. Numerous aminoacids are formed when acetaldehyde is irradiated instead of formaldehyde. In this case lysine, ornithine, arginine, glutamic acid, tyrosine, valine, leucine, and isoleucine were also found (Table 2).

The mechanism of the synthesis of aminoacids when gaseous mixtures of methane, ammonia, and other components are acted upon by ultraviolet radiation has been less thoroughly investigated. Presumably photolysis results in the formation of radicals analogous to those examined previously. For example, the photodissociation of methane does not stop at the stage involving the formation of the CH_3 radical, but very probably proceeds further to CH_2 and CH.[124] The quantum yield of ammonia reactions such as $NH_3 \rightarrow NH + H_2$ and $NH_3 \rightarrow N + H_2 + H$ increases with decrease of wavelength[125]. The recombination of various radicals can lead to the formation of aminonitriles.

Sidorov[126] and Pavlovskaya and coworkers[123] proposed a mechanism for the synthesis of aminoacids from aldehydes and ammonium salts under the influence of ultraviolet radiation. In the presence of formaldehyde, the $CH\dot{O}$ radical is formed initially, its recombination giving rise to glyoxal. The latter is converted under the influence of a light quantum into glyoxalic acid, which in the presence of ammonia and hydrogen gives rise to the simplest aminoacid—glycine. In the presence of higher aldehydes, other intermediate products are possible (ketoacids), which are transformed into more complex aminoacids.

The non-biologically synthesised aminoacids can themselves undergo interconversions. Thus, when valine is irradiated with ultraviolet light in the presence of metal oxides (ZnO and V_2O_5), glycine, threonine, and alanine are formed[127]. Alanine and glycine have been obtained from leucine under these conditions. In aqueous aminoacid solutions without metal oxides, new aminoacids are not formed. It is interesting that in the presence of MoO_3 irradiation of alanine or leucine leads to the formation of more complex aminoacids, for example, aspartic acid[128]. However, such acids are not formed from glycine. The photolysis of phenylalanine in the presence of polyphosphoric acid leads to its decomposition and hydroxylation, which results in the formation of tyrosine, alanine, and glycine[129]. In addition to the new aminoacids, ammonia, aldehydes, and carboxylic acids are formed under the conditions of the experiments.

c. Thermal Syntheses

The heat necessary for chemical synthesis on Earth might have been provided by early volcanic activity, which was probably much greater than at the present time. The wide distribution of regions in which thermal waters emerge on the surface suggests that the heat derived from thermal sources might have been important for the formation of aminoacids.

In order to investigate the possibility of the formation of biologically important compounds from gases evolved by magmatic rocks, Harada and Fox[130] heat-treated a mixture of methane, ammonia, and water. The initial gaseous products were passed at a high rate through a quartz tube heated to 900–1000°C. The tube was filled with silica gel, alumina gel, or volcanic lava. The reaction products were absorbed with aqueous ammonia and then hydrolysed (4 *N* HCl). Aminoacid analysis demonstrated the formation of a large proportion of protein aminoacids, including aromatic aminoacids, namely, aspartic and glutamic acids, threonine, serine, proline, glycine, alanine, valine, leucine, isoleucine, tyrosine, and phenylalanine. β-Alanine and certain other non-natural aminoacids were also detected.

This experiment aroused interest among investigators and was frequently repeated for a detailed investigation of the conditions of the synthesis and the composition of the aminoacids. Thus, Taube et al.[131] largely confirmed the results of Harada and Fox. Apart from the compounds indicated above, they identified lysine in the reaction mixture by electrophoresis. Oró[132,133], who carried out a similar experiment in the absence of a catalyst, showed that the same set of aminoacids is formed. Glycine and alanine had the highest concentrations in the mixture (Table 2). The reaction mixtures obtained under the conditions of the experiments of Harada and Fox[130] were recently analysed[134] by gas chromatography and mass spectrometry. It was shown that aminoacids are formed in low yields (0.007%) and fewer were found than in the experiment of Harada and Fox[130]. The authors note that β-aminoacids predominate in the mixtures.

Comparison of the experiments with the effect of electric discharges and heat on gaseous mixtures showed that the simplest aminoacids (glycine and alanine) are formed in maximum amounts regardless of the type of energy used.

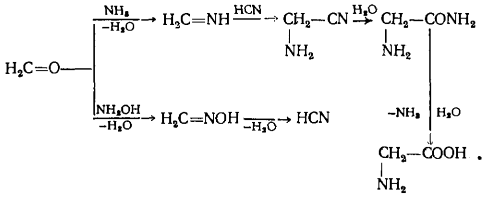
Aspartic and glutamic acids have been obtained in high yields by the thermal method. Reactions involving the isomerisation of the hydrocarbon chain (valine, leucine, and isoleucine are present in the mixture), cyclisation (tyrosine, phenylalanine, and proline), and hydroxylation (threonine, serine, and tyrosine) are more characteristic of thermopyrolysis. An increase of temperature favours these reactions[132,133]. Reactions involving the formation of unbranched chains (aminobutyric acid, sarcosine, and methylalanine) are more probable in electropyrolysis. It is noteworthy that the action of heat leads to the formation of mainly natural aminoacids.

It has been established that non-biological synthesis takes place at the present time and might have occurred in the remote past in the film on the edge of thermal sources and in the eruption of volcanoes[85,135]. Fox[136] analysed lava specimens collected with sterile steel rods in the eruption of Mauna Loa volcano (Hawaian Islands). The lava temperature during sampling exceeded 1000°C. The specimens were treated with hot water and the aqueous extract was hydrolysed (6 *N* HCl). Aminoacid analysis revealed the presence of 16 aminoacids (Table 2) with an overall yield of about 30×10^{-9} mole/g of lava. Glutamic (27%) and aspartic (12.5%) acids as well as glycine and alanine (16.8 and 10.0% respectively) were present in largest amount. It is interesting that a sulphur-containing aminoacid (methionine) was also detected in the mixture. The cooled lava had a bubble structure and consequently contained gas. Fox believes that the aminoacids were synthesised from the gases during their cooling.

Non-biological aminoacid mixtures can be obtained from CO, H_2, and NH_3 under the conditions of a modified Fischer–Tropsch process[25,137–139]. The initial mixtures of gaseous products were heated to 150–700°C in the presence of a wide variety of catalysts (montmorillonite, alumina gel, or silica gel). The resulting mixture contained a large proportion of protein aminoacids, including structurally complex aromatic and heterocylic aminoacids (Table 2), the yield of which was 0.01–0.1%.

Bakh was one of the first to use formaldehyde and hydrocyanic acid in thermal synthesis of non-biological aminoacids and polypeptides[9]. By heating (80–100°C) aqueous mixtures of hydrocyanic acid and ammonia or formaldehyde and hydroxylamine, it is possible to obtain the following aminoacids[133]: glycine, alanine, aspartic and glutamic acids, serine, threonine, leucine, isoleucine, arginine, α-amino-n-butyric and $\alpha\beta$-diaminopropionic acids, and β-alanine. In the latter mixture, a considerable amount of glycine is formed. When hydroxylamine is replaced by hydrazine, certain aminoacids are again synthesised. Simple heating of an aqueous solution of formaldehyde with ammonia (3 : 1) followed by acid hydrolysis (185°C, 8 h) led to the formation of a mixture of aminoacids[140,141], which qualitatively differed little from the mixture obtained by Pavlovskaya and coworkers[121,122]. The quantitative proportions of the aminoacids are indicated in Table 2. Their overall yield was 0.007%. Hexamethylenetetramine was detected in the reaction product. The reaction has also been achieved in the presence of lunar dust[136]. After hydrolysis, six aminoacids were detected, the amounts of glycine and glutamic acid being greatest.

The synthesis of aminoacids on heating formaldehyde and ammonia[140,141] proceeds via hexamethylenetetramine[142], the formation of which from these starting materials was first demonstrated by Butlerow[43]. The acid hydrolysis of hexamethylenetetramine also yielded all the aminoacids synthesised from CH_2O and NH_3.[142] Oró[144] suggests that aminoacids are formed in thermal syntheses from a mixture of formaldehyde, hydroxylamine, and water via oximes, hydrocyanic acid, and aminoacid amides. For example, the following reaction mechanism is possible in the case of glycine:



The high reactivities of aminonitriles, which are important aminoacid precursors, has been noted in the literature. Thus Moser and Matthews[145] reported that certain α-aminoacids are formed on neutral or alkaline hydrolysis of aminoacetonitrile. They believe that aminoacids are synthesised via the decomposition of aminoacetonitrile to HCN and NH_3, the polymerisation of HCN, and subsequent hydrolysis of the polymer to various aminoacids.

In the presence of CH_2O, aminoacetonitrile can give rise to methyleneaminoacetonitrile, which is also readily formed from CH_2O, HCN, and NH_4OH.[146] This compound is converted on mild hydrolysis (110°, pH 5.5–10) into glycine, serine, hydroxymethylserine, alanine, sarcosine, and di- and tri-glycine. It has been suggested that glycine and formaldehyde are the products of the direct hydrolysis of methyleneaminonitrile, while serine and hydroxymethylserine are obtained on *C*-hydroxymethylation of the reactive methylene group of the initial compound (or of the glycine formed) by formaldehyde. Alanine is probably formed from serine via dehydroalanine.

In order to elucidate the mechanism of the synthesis of complex aminoacids, it is quite justifiable to attempt to use as starting materials the simplest aminoacids or their derivatives, which are obtained in high yields in most non-biological syntheses. Thus, the synthesis of valine and isoleucine, aminoacids with branched hydrocarbon chains, is probably based on the fairly high yield of the nitrile of glycine formed on cyanide polymerisation[112]. The nitrile gives rise to the required aminoacids in the presence of acetone or ethyl methyl ketone (40°C, 21 days)[147]. The yield of valine is 0.3% and that of isoleucine is lower by an order of magnitude. Ketones are believed to be the products of non-biological syntheses, since they can be obtained from the corresponding acetylene homologues.

The possibility of the formation of serine by the reaction of glycine with formaldehyde (60–100°C, phosphate buffer) has been demonstrated[147]. It was shown that formaldehyde exhibits catalytic activity. Apart from serine, hydroxymethylserine, sarcosine, alanine, and iminodiacetic acid may be obtained from dilute alkaline solutions of glycine and formaldehyde[148]. The introduction of acetaldehyde or benzaldehyde leads to the synthesis of threonine or β-phenylserine respectively.

The most complex aminoacid (tryptophan) was obtained by the Michael reaction (60–100°C, 8–53 days) from indole and dehydroalanine employed in the form of a peptide to increase its stability[147]. The yield of tryptophan was between 0.01 and 0.5%. Indole, formed in small amounts in electric discharges from hydrocarbons and ammonia, can also be regarded as a precursor of tryptophan.

d. Other Syntheses

There have been fewer studies in which prebiological syntheses of aminoacids under the influence of ionising radiation were investigated. However, they confirm to a large extent the results obtained by the procedures discussed above. Palm and Calvin[149] irradiated with fast electrons in a linear accelerator (5 MeV, overall dose 10^9 rad, 6 ms pulses at a frequency of 30 Hz) a gaseous mixture of CH_4, NH_3, and H_2O, which was kept over an ammonia solution of magnesium and iron silicate or ammonium phosphate; the experimental temperature was 30–80°C. Analysis of the liquid phase by ion-exchange and paper chromatography demonstrated the formation of a multiplicity of products: aminoacids (glycine, alanine, and aspartic acid), hydrocyanic and lactic acids, urea, C_3–C_6 sugars, etc. Unfortunately, the gas phase was not analysed.

Studies by Oró[133] confirmed and extended these experiments. A similar mixture was irradiated under identical conditions and the same aminoacids were detected by paper radiochromatography. In addition, glycine amide was identified. Oró also reported a novel method for irradiating with fast electrons a solid mixture of CH_4, NH_3, and H_2O at the liquid nitrogen temperature. The aim of the experiment was to simulate the irradiation of the nucleus of a comet in space. Similar aminoacids were detected in the aqueous phase[149], but their radiochemical yields could not be found owing to the lack of analytical data for the gaseous phase.

Choughuley and Lemmon[150] demonstrated the possibility of synthesising sulphur-containing aminoacids on irradiation of a mixture of CH_4, NH_3, H_2O, and H_2S with fast electrons. Nevertheless, it was difficult to obtain them in satisfactory yields under such conditions owing to the ease of oxidation of the mercapto-groups by the water radiolysis products.

Studies on the synthesis of aminoacids from a mixture of gases (CH_4, NH_3, H_2O, N_2, and CO_2) under the influence of low-intensity X-rays have been carried out[151]. Electrophoretic analysis of the aqueous extracts of the radiolysis products demonstrated the formation of neutral and acid aminoacids as well as amines. In subsequent similar investigations[152], glycine, alanine, and aspartic acid were found. The radiochemical yields of the aminoacids were low owing to the low selectivity of the process. Furthermore, one may note that the radioactivity might possibly have supplied energy for the synthesis of aminoacids mainly on the surface of the primitive Earth and not in the atmosphere.

Aminoacids can also be obtained in the field of ultrasonic waves[153]. Aqueous solutions of organic acids, formed by the Miller electrosynthesis[3], saturated with molecular nitrogen or a nitrogen–hydrogen mixture served as the starting materials. The formation of aminoacids was also observed following the exposure of ammonium chloride solutions containing urea or hydroxylamine to ultrasound. Experiments have been carried out recently using the energy of a shockwave[154–156]. Similar conditions are likely to have occurred on collision of meteorites with Earth's atmosphere. A number of aminoacids obtained from the gaseous mixture were identified in these experiments.

The aim of the studies considered in this section was to investigate mainly the possibility of the prebiological synthesis of protein aminoacids, i.e. to investigate one of the first steps in chemical evolution on Earth. Considerable advances have been made in this field. Almost all the protein aminoacids and a series of non-protein aminoacids have been synthesised. It is interesting that, regardless of the type of energy employed, various methods of non-biological synthesis lead to the formation of similar sets of aminoacids, in which there are many protein aminoacids. The analytical procedure developed recently makes it possible to detect a very large number of aminoacids present simultaneously in the mixtures synthesised.

The data quoted suggest that the problem of determining the principal pathways in the prebiological synthesis of aminoacids under laboratory conditions may be regarded as to a large extent solved. The possible discovery of new non-biological methods for their formation will confirm yet again the wide variety of natural pathways to the origin of life on Earth. The mechanism of the chemical conversion of simple starting materials into aminoacids, products with a highly developed polyfunctional structure, has many aspects, which are still unelucidated despite the large number of studies carried out. This applies particularly to the reactions occurring under the influence of ionising radiation, ultraviolet light, and heat, although in each case, including reactions under the influence of electric discharges, the excitation, activation, and ionisation processes have much in common, which is confirmed by the similarity of the products synthesised. In this connection, consistent efforts of investigators in the field of non-biological syntheses will probably be directed to a more systematic elucidation of the mechanisms of the formation of aminoacids.

It is interesting that all the protein and non-protein aminoacids discovered in the Murchison meteorite have been identified in a single experiment using electric discharges. There is a similarity not only between the qualitative but also the quantitative compositions of the products obtained in the laboratory experiment and discovered in the meteorite. One must emphasise yet again that the carbonaceous material in meteorites contains both aminoacids and their precursors—formaldehyde, hydrogen cyanide, and cyanoacetylene, i.e. compounds which are obtained in various non-biological syntheses. Together with the results of the analysis of lunar rocks, these data constitute evidence for universality of the prebiological pathways to the formation of aminoacids.

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Condensed Tetrazoles

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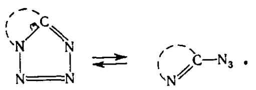
The present review surveys the literature on the methods of synthesis and chemical properties of condensed tetrazoles. The bibliography includes 125 references.

CONTENTS

I. INTRODUCTION

During the last 15 years, numerous studies dealing with the structure and properties of condensed tetrazoles have been published, the reason being that the tetrazole ring condensed via the $N_{(1)}-C_{(5)}$ bond with other rings exhibits a number of characteristic features in relation to non-condensed 1,5-disubstituted tetrazoles. Conversions into isomeric 2-azido-derivatives of nitrogen-containing heterocycles, which frequently occur on heating solutions of the test substance and sometimes in the crystalline state after prolonged storage, are characteristic of such condensed systems:

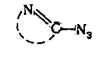


An equilibrium is then frequently established between the isomeric tetrazole and azido-forms, the position of which depends on the electronic nature of the condensed ring and its substituents, the polarity of the solvent, the pH of the medium, the reaction temperature, and the nature of the reagent employed[1].

Certain methods for the synthesis and the properties of individual examples of this interesting type of compound have been described in reviews dealing with the azide–tetrazole tautomerism[1-6], but a review in which methods for the synthesis of condensed tetrazoles and the relations between their properties and structures are surveyed and described systematically is lacking. The literature data on this problem are discussed in the present article (including publications in 1973).

II. METHODS FOR THE SYNTHESIS OF CONDENSED TETRAZOLES

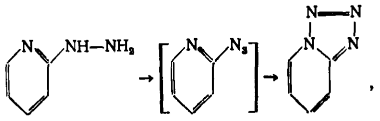
The majority of the reactions leading to condensed tetrazoles proceed via the formation of isomeric α-azido-derivative of nitrogen-containing heterocycles as intermediates. In this case the group



may be compared with the azidoazomethine group $R_2-N=\underset{R_1}{\underset{|}{C}}-N_3$ in linear systems, which isomerises irreversibly to the thermodynamically more stable tetrazole ring. Calculations carried out by Roberts[7] have shown that an appreciable expenditure of energy is not required for the formation of the tetrazole ring on formation of a bond between the azido-group and a nitrogen atom in an open chain or a ring.

If the azidoazomethine group is part of a heterocycle, the formation of a bond between the azido-group and the nitrogen atom of the heterocycle and the consequent formation of a condensed system do not always occur. Depending on the nature of the nitrogen-containing ring and the electronic nature of the substituents, the reaction product may be isolated in the form of a condensed tetrazole isomeric with the azido-derivative or in the form of an equilibrium mixture of both tautomeric forms.

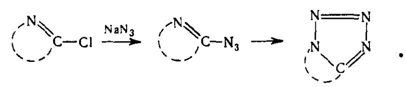
One of the most widely used methods for the synthesis of condensed tetrazoles involves the interaction of α-hydrazino-derivatives of nitrogen-containing heterocycles with nitrous acid. Tetrazolo[5,1-*a*]pyridine (I) was obtained for the first time by this procedure in 1915[8]:



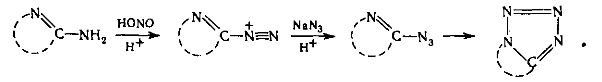
(I)

and subsequently compounds were synthesised in which the tetrazole ring is condensed with isoquinoline[9], quinoxaline[10-12], *s*-triazine[13], pyrimidine[14-18], phthalazine[19-22], naphthothiazole[23], pyridazine[24-26], pyrazine[26], pyridine[27], naphthyridine[28-35], uracil[36], quinoline[37,38], quinazoline[10,39,40], purine[41,42], thiazole[43-45], and benzoselenazole[46,47].

Condensed tetrazoles are frequently obtained by the interaction of α-chloro-derivatives of nitrogen-containing heterocycles with nitrous acid or sodium azide in a solvent (alcohol, acetonitrile, dimethylformamide). α-Chloroderivatives of benzothiazole[48], pyridine[49-53], quinoline[54], pyridazine[25,26,55-57], pyrimidine[14,15,58,59], quinazoline[14,22,40,60-62], phthalazine[19-22], quinoxaline[10,19], pyrazine[63], triazine[26], and naphthyridine[30,32] have been introduced into this reaction:



A convenient modification of this method involves the diazotisation of *α*-amino-derivatives of nitrogen-containing heterocycles followed by treatment of the resulting diazonium salts with sodium azide in an acid medium[48,64-66]:

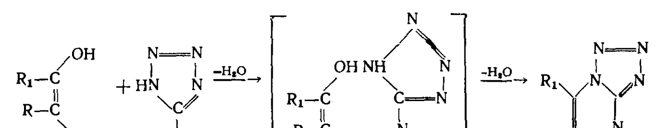


Although the yield of tetrazoles is lower in this case than in the synthesis by the procedures described above, the amino-derivatives are sometimes more readily available than the chloro- or hydrazino-derivatives. Furthermore, certain condensed tetrazoles cannot be formed at all by the first two methods. Thus, instead of the expected thiazolo[2,3-*e*]tetrazole, the interaction of 2-hydrazinothiazole with nitrous acid led to the isolation of 2,2′-dithiazolyltriazene[14]. On the other hand, the required product can be readily obtained from 2-aminothiazole[67]. Consequently this method was later used by Carboni and coworkers to synthesise tetrazolonaphthyridines[31,35].

Condensed tetrazoles can also be obtained by carrying out the Schmidt reaction with cyclic ketones. 1,5-Pentamethylenetetrazole[68], adamantane derivatives[69], methylcyclohexanone and camphor derivatives[70-72], and others[69] have been obtained by this method. Ruzicka and coworkers applied this reaction to higher cyclic ketones—cyclopentanone, cyclooctanone, cyclopentadecanone, and civetone[73,74]. The reaction of nitrous acid with 2-methoxy-Δ^1-pyrroline, as a result of which a compound which is probably trimethylenetetrazole was isolated, has been reported[75].

By treating 3,3-dihalogenoazocycloalkan-2-ones with phosphorus pentachloride and subsequent treatment of the resulting intermediate iminochlorides with nitrous acid, 8,8-dichloro- and 8,8-dibromo-tetrahydrotetrazolo[1,5-*a*]pyrimidines, 9,9-dichloro- and 9,9-dibromo-6,7,8,9-tetrahydro-5*H*-tetrazolo[1,5-*a*]azepines, and 10,10-dichloro-5,6,7,8,9,10-hexahydrotetrazolo[1,5-*a*]azocine have been obtained[76].

Several examples of the synthesis of condensed tetrazoles using non-condensed tetrazoles as the starting materials have been described. Derivatives of tetrazolo[1,5-*a*]pyrimidine (II) have been obtained by the reaction of 5-aminotetrazole with *β*-diketones or *β*-keto-acids[77]:



(II)

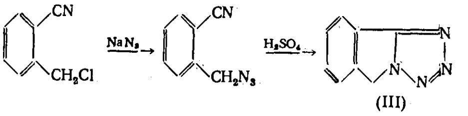
where

$R = H,\ R_1 = CH_3,\ R_2 = OC_2H_5;$
$R = H,\ R_1 = R_2 = CH_3;\ R = H,\ R_1 = C_6H_5,\ R_2 = CH_3,$
$R = R_1 = R_2 = CH_3.$

The mechanism of this reaction has been studied by Temple and Montgomery[16], who showed that the intermediate may be isolated as the sodium salt. Other tetrazolopyrimidines have been obtained by the same procedure[17,78,79].

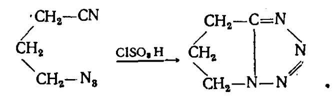
A series of chemical transformations led to the conversion 1-(*o*-carboxyphenyl)-5-phenyltetrazole into 1-(*o*-aminophenyl)-5-phenyltetrazole, which yields tetrazolophenanthridine on treatment with nitrous acid[54]. Certain tetrazolopyridines and isoquinolines have been synthesised by the dehydrogenation of 1-(*α*-pyridyl)-3-aryltriazine with tribromophenyl bromide in acetic acid at room temperature[36].

When azidonitriles are treated with concentrated acids, condensed tetrazoles are also formed[80-82]. Thus 5*H*-tetrazolo[1,5-*a*]isoindole (III)[82] has been obtained by the reaction of *o*-chloromethylbenzonitrile with sodium azide in aqueous alcoholic medium followed by the treatment of the resulting *o*-azidomethylbenzonitrile with concentrated sulphuric acid while cooling the mixture:



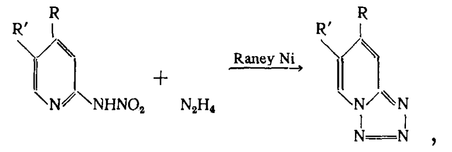
(III)

When chlorosulphonic acid is allowed to react with *γ*-azidobutyronitrile, trimethylenetetrazole is formed[81] (IV):



(IV)

A method has been proposed for the preparation of substituted hydrogenated derivatives of (I) from nitraminopyridines and hydrazine in the presence of Raney nickel[83]:



$R = R' = H;\ R = CH_3,\ R' = H;\ R = H,\ R' = CH_3.$

III. THE PROPERTIES OF CONDENSED TETRAZOLES

The reactions in which condensed tetrazoles participate may involve the condensed tetrazole ring or the isomeric azidoazomethine group, the heterocycle with which the tetrazole ring is condensed, or a substituent in the heterocycle.

The chemical properties of condensed tetrazoles depend on the stability of the tetrazole ring, the type of reactant, and the reaction conditions. The first stage of these reactions frequently involves the opening of the tetrazole ring and the formation of the isomeric azidoazomethine derivative under the influence of heat, the solvent, or another reactant. The condensed tetrazole then reacts like an aromatic or heterocyclic azide. The reaction may be accompanied by the evolution of nitrogen and the subsequent recombination of the nitrene radicals formed (photolysis and thermolysis). Interaction with nucleophilic reagents leads to the substitution of the azido-group (reactions with sodium cyanide and organometallic compounds). Reactions which proceed via the cycloaddition of the azido-group formed have also been described.

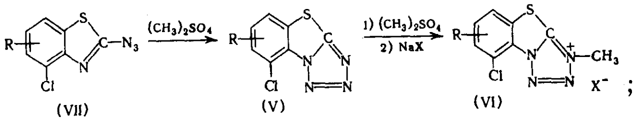
If the tetrazole ring shows no tendency towards isomerisation or is stabilised under the reaction conditions, it is preserved.

1. The Effect of Inorganic Acids and Alkylating Agents

The effect of inorganic acids on condensed tetrazoles depends on the nature of the nitrogen-containing heterocycle with which the tetrazole ring is condensed. Strong inorganic acids and trifluoroacetic acid at room temperature sometimes increase the stability of the tetrazole ring and displace the azide–tetrazole equilibrium towards the cyclic form. At the same time the electron-accepting tetrazole ring is protonated.

Thus Pochinok and coworkers[84] showed that tetrazolo-[5,1-*b*]-benzothiazole (V), thiazolo[3,3-*e*]tetrazole, and their derivatives with electron-donating substituents dissolve in concentrated sulphuric acid without decomposition, the dissolution being accompanied by protonation. When the solution is diluted with water, the initial tetrazoles are recovered almost quantitatively. Furthermore, when certain isomeric 2-azido-derivatives, for example 2-azido-4-chloro-benzothiazole, are dissolved in inorganic acids, they isomerise to condensed tetrazoles with subsequent protonation of the resulting ring[84]. The increase of the stability of the tetrazole ring of tetrazolo[5,1-*a*]pyridine (III) in an acid medium has also been reported by Boyer et al.[85] This compound does not decompose even on heating in concentrated acid up to 120°C.

When tetrazolo[5,1-*b*]benzothiazoles (V) react with dimethyl sulphate or triethyloxonium fluoroborate, the condensed tetrazole ring is alkylated with formation of quaternary tetrazolium salts (VI) and not the isomeric azidinium salts[84]. For example, alkylation of 2-azido-4-chlorobenzothiazole (VII) proceeds via the preliminary isomerisation to the 8-chloro-derivatives (V) under the influence of polar dimethyl sulphate:

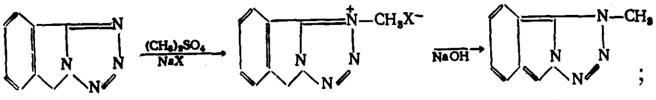


(VII) (V) (VI)

$X = I, ClO_4$.

By subsequent treatment with a saturated alcoholic solution of sodium iodide or sodium perchlorate, the *N*-methyltetrazolium methyl sulphates were converted into the corresponding methiodides or methoperchlorates.

Under analogous conditions compound (III) has been converted into a quaternary salt, from which the base (VIII) was obtained on treatment with alkali[82]:

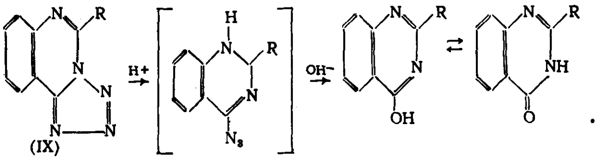


(III) (VIII)

$X = ClO_4, I$.

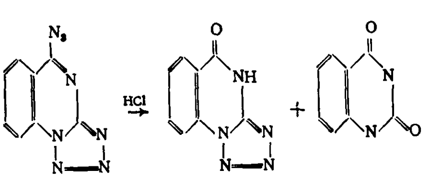
If the nitrogen-containing heterocycle can be protonated, electrons are withdrawn from the tetrazole ring, the stability of the latter decreases sharply, and the azide–tetrazole equilibrium in the system is displaced towards the isomeric azido-form[15,16,26,31,34,52,85] in which the azido-group plays the role of the electron donor.

On heating in acids, the azido-group produced is hydrolysed and replaced by the hydroxy-group. Postovskii and coworkers showed[40,56,62] that heating of 5-substituted tetrazolo[1,5-*c*]quinazolines (IX) in hydrochloric acid leads to the formation of 2-substituted 4-quinazolinones. This process can be assumed to involve a stage in which the condensed tetrazole ring is opened with subsequent hydrolytic abstraction of the azido-group via a nucleophilic mechanism:



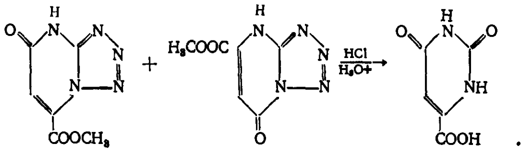
(IX)

When the 5-azido-derivative (X), in which the tetrazole ring is somewhat more stable, is heated in hydrochloric acid, a mixture of tetrazolo[1,5-*a*]quinazolin-5-one (XI) and quinazoline-2,4-dione (XII) is formed:



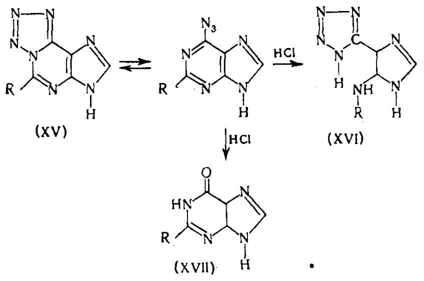
(X) (XI) (XII)

It has been found[87] that, when a mixture of the isomers of methoxycarbonyloxodihydrotetrazolo[1,5-*a*]pyrimidine (XIII) is refluxed with hydrochloric acid, 1,5-dipolar opening of the tetrazole ring also takes place with subsequent nucleophilic substitution of the azido-group and the formation of 6-carboxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidine (XIV):



(XIII) (XIV)

Temple et al.[42] found that the unsubstituted 6-azidopurine system (XV, R = H) is converted preferentially into 5-substituted tetrazole (XVI) on treatment with concentrated hydrochloric acid:



(XV) (XVI) (XVII)

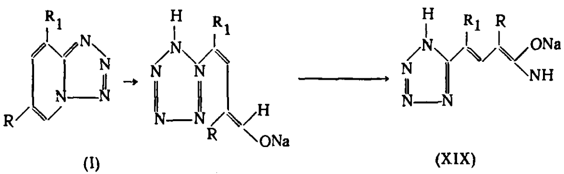
When an amino- or chloro-group is present in the 2-position [compounds (XV, R = NH_2 or Cl)], the system is resistant to the action of hydrochloric acid at room temperature, but hydrolyses on heating to guanine or xanthine (XVII).

2. The Effect of Alkalis and Alkoxides

Condensed tetrazoles, which as a rule readily undergo ring opening under the influence of acids, are more stable in alkalis and do not interact with them[31,34]; the nitrogen-containing heterocycle is cleaved[16,42,88,89].

Carboni and coworkers[31,34] showed that in the hydroxy- and amino-derivatives of substituted tetrazolo[1,5*a*][1,8]-naphthyridines (XVIII) the tetrazole formed is stabilised by alkalis. When the acetamido-derivative (XVIII) is hydrolysed with sodium hydroxide, the amino-derivative is formed in satisfactory yield, the tetrazole ring being unaffected[29–33].

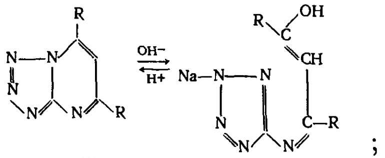
Derivatives of tetrazolo[5,1-*a*]pyridine (I) with electron-donating substituents in the 6- and 8-positions readily dissolve in alkalis, alkoxides, or organic bases[88]. The pyridine ring is then opened with formation of the 5-substituted tetrazole (XIX) and its subsequent *cis-trans* isomerisation:


(I) (XIX)

R=NO$_2$.

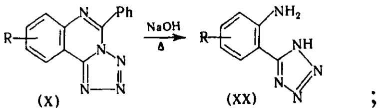
The cleavage of the nitrogen-containing heterocycle in condensed tetrazoles under the influence of alkali has been described for tetrazolo[1,5-*a*]pyrimidines[16] (II), tetrazolo[1,5-*a*]quinazolines (X)[89], and the 6-azidopurine (XV) system[42].

When compound (II) or its dimethyl derivative is dissolved in 0.1 *N* aqueous solution of alkali, the product is an equilibrium system which is reconverted into (II) on cautious acidification[16]:


(II)

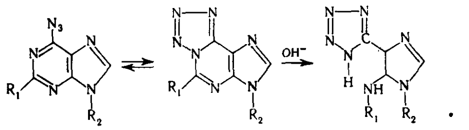
R=H, CH$_3$.

Golomolzin and Postovskii[89] described the alkaline cleavage of 5-phenyl-7(9)-R-tetrazolo[1,5-*c*]quinazolines (X), which results in the formation of 5-[2-amino-3′(5′)-R-phenyl]tetrazoles (XX):

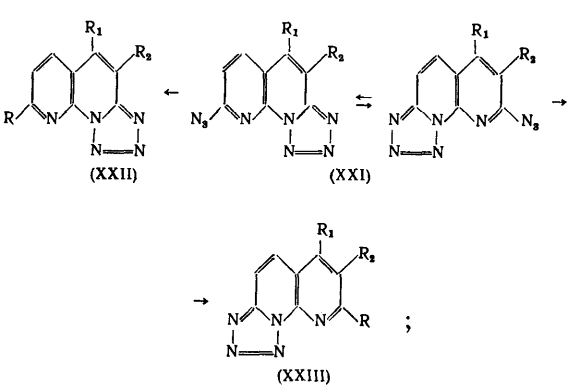

(X) (XX)

R=H, OCH$_3$, CH$_3$, Cl, Br.

The pyrimidine ring is opened similarly when the system (XV) substituted in the 2-position is treated with aqueous solutions of alkali[42]:


(XV) (XVII)

The tetrazole ring is also retained in the azido-derivatives of condensed tetrazoles 6-azidotetrazolo[1,5-*b*]pyridazine[25], 6-azidotetrazolo[1,5-*a*]phthalazine[99], 6-azidopyrido[2,3-*d*]tetrazolo[5,1-*b*]pyridazine[91], 6-azidopyrido[3,2-*d*]tetrazolo[1,5-*a*][naphthyridine[29-33], 6-azidopyrazino[2,3-*d*]tetrazolo[4,5-*b*]pyridazine[92], and 5-azidotetrazolo[1,5-*a*]quinazoline[62] on heating with aqueous or alcoholic solutions of alkalis, alkoxides, ammonia, and organic bases. The azido-group is activated under the influence of the electronegative tetrazole ring and readily becomes involved in a nucleophilic substitution reaction, which results in the formation of the corresponding hydroxy-, alkoxy-, amino-, and hydrazino-derivatives of the condensed tetrazoles. Mixtures of the isomeric hydroxy- and alkoxy-derivatives (XXII) and (XXIII) are formed from substituted 8-azidotetrazolo[1,5-*a*][1,8]-naphthyridines (XXI), which exist in solution in the form of two isomeric species in equilibrium[29-33]:


(XXII) (XXI)

(XXIII)

R=OH, OC$_2$H$_5$, NH$_2$

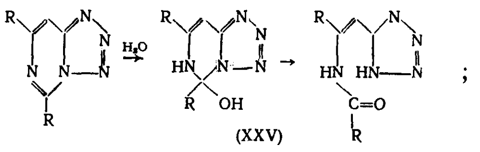
R$_1$=R$_2$=H; R$_1$=CH$_3$, R$_2$=H; R$_1$=C$_6$H$_5$, R$_2$=H;

R$_1$=H, R$_2$=CH$_3$.

3. Covalent Hydration

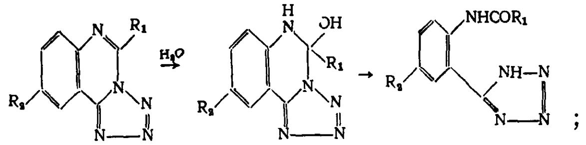
The condensation of the electron-accepting tetrazole ring with pyrimidine, purine, or quinazoline leads to the withdrawal of electrons from the carbon atom in the 5-position as a result of which there is a possibility of the formation of covalent hydrates involving the N$_{(6)}$–C$_{(5)}$ bond. The covalent hydration process competes with the cleavage of the nitrogen-containing ring, leading to the formation of 5-substituted tetrazoles, the former process predominating. The stability of covalent hydrates is greatly influenced by the pH of the medium, the electronic nature of the substituents in the nitrogen-containing heterocycle, and temperature.

Thus it has been shown[58] that tetrazolo[1,5-*c*]pyrimidine (XXIVa) readily reacts with water to form the covalent hydrate (XXVa), which cannot be dehydrated even on heating *in vacuo* to 120°C. The 5,7-dimethyl derivative (XXIVb) forms a covalent hydrate even at room temperature, but this involves the opening of the pyrimidine ring and the formation of the substituted tetrazole (XXVIb)[15]:


(XXIV) (XXV) (XXVI)

(a) R=H; (b) R=CH$_3$.

A similar process involving (XXIV) proceeds in an alkaline medium with formation of a salt. The 2-azidopurine system (XV) also undergoes covalent hydration[42]. It has been shown in a series of studies by Postovskii and coworkers[93-97] that the covalent hydration of tetrazolo-[1,5-*c*]quinazolines (X) takes place in a weakly acid medium, since the protonation of the N$_{(6)}$ heteroatom promotes an increase of δ^+ on the C$_{(5)}$ atom[96] and the yield of such interaction depends on the nature of the substituents. The unsubstituted tricyclic compound (Xa) is hydrated more readily than the 5-methyl derivative (Xb), while the 5-phenyl analogue (Xc) is not hydrated at all:



(X) (XXVI)

(a) $R_1=R_2=H$; (b) $R_1=CH_3$, $R_2=H$; (c) $R_1=C_6H_5$, $R_2=H$;
(d) $R_1=\gamma$-pyridyl , $R_2=H$; (e) $R_1=C_6H_5$, $R_2=COOH$;
(f) $R_1=C_6H_5$, $R_2=Br$.

It may be that the steric hindrance associated with the phenyl group also plays a role here. The 5-γ-pyridyl derivative (Xd) behaves similarly[95,96]. The introduction of a carboxy- or bromo-group, which increase the positive charge on $C_{(5)}$, into the 9-position of compound (Xc) makes possible the hydration of compounds (X,e and f)[93,97]. The product of the hydration of (Xf) has the structure of 5-(2-acylamino-5-bromophenyl)tetrazole (XXVII) in the crystalline state[94].

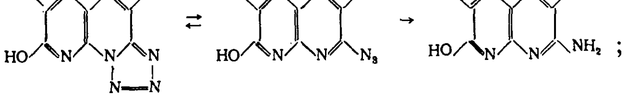
When the covalent hydrates are heated in 2 *N* hydrochloric acid, acid hydrolysis takes place with formation of 5-(2-acylaminophenyl)tetrazoles[95,96].

4. Reduction

The resistance of the condensed tetrazole ring to the action of reducing agents or catalytic hydrogenation depends in many respects on the reaction conditions, particularly on the pH of the medium. Boyer et al.[85], who investigated the catalytic hydrogenation of tetrazolo[5,1-*a*]pyridine (I), showed that in an acid medium, where the tetrazole form (I) is stabilised, only the pyridine ring is hydrogenated. 2-Aminopyridine is formed in an alkaline medium. In a neutral medium the reaction proceeds in two ways with formation of a mixture of products. They also observed that, when the 6-methyl-4-nitro-derivative of (I) is treated with stannous chloride in hydrochloric acid, only the nitro-group is reduced.

In those cases where a second nitrogen heteroatom in the nitrogen-containing heterocycle is protonated, the stability of the condensed tetrazole ring is reduced and acids and bases are found to have the opposite effects on the mode of catalytic hydrogenation.

Carboni and coworkers[31,34] showed that, in the case of the isomeric hydroxy-derivatives of 5(6)-phenyltetrazolo-[1,5-*a*][1,8]naphthyridine (XXVIII), the azido-form is stabilised (as a result of protonation) by acids and the tetrazole form is stabilised by alkalis. Accordingly, during the catalytic hydrogenation of (XXVIII, a – d) in acetic acid, amino-derivatives of naphthyridine (XXIX) are formed in acetic acid in 75–78% yield. After hydrogenation in an alkaline medium, the initial compounds (XXVIII), a – d) were recovered in an almost quantitative yield:

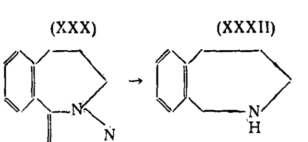


(XXVIII) (XXIX)

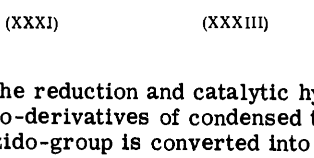
(a) $R_1=C_6H_5$, $R_2=R_3=R_4=H$; (b) $R_1=R_3=R_4=H$; $R_2=C_6H_5$;
(c) $R_1=R_2=R_4=H$, $R_3=C_6H_5$; (d) $R_1=R_2=R_3=H$, $R_4=C_6H_5$.

Tetrazolo[1,5-*a*]pyrimidines behave similarly on hydrogenation in acetic acid[98].

The reduction of pentamethylenetetrazole (XXX) and 6,7-dihydro-5*H*-tetrazolo[4,5-*a*]benzo[*c*]azepine (XXXI) with lithium aluminium hydride in isopropyl ether, leading to the formation of the perhydroazepine (XXXII) and 1,2,3-tetrahydrobenzo[*c*]azepine (XXXIII) has been described[72]:



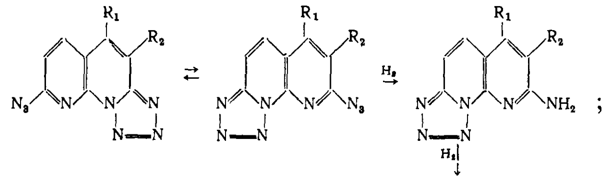
(XXX) (XXXII)



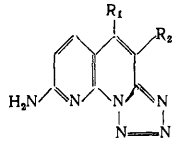
(XXXI) (XXXIII)

The study of the reduction and catalytic hydrogenation reactions of azido-derivatives of condensed tetrazoles has shown that the azido-group is converted into the amino-group much more readily than the condensed tetrazole ring. Thus, hydrogenation, treatment with hydrogen sulphide, or heating in ethylcellosolve of 6-azidotetrazolo-[1,5-*b*]pyridazine[22,25] and heating of 6-azidotetrazolo-[1,5-*a*]phthalazine in tetralin[22] leads to the formation of the corresponding aminotetrazoles.

Catalytic hydrogenation of the unsubstituted 8-azidotetrazolo[1,5-*a*][1,8]naphthyridine (XXIa) results in the formation of the 8-amino-derivative and a very small amount of the 8-hydroxy-analogue[29]. Under these conditions, the 5-methyl and 5-phenyl derivatives (XXI, b and c) are preferentially converted into the corresponding amines (XXXIV, b and c) and their 4-methyl and 4-phenyl analogues (XXI, d and e) are converted into the amines (XXXV, d and e)[31-34]:



(XXI) (XXXIV)

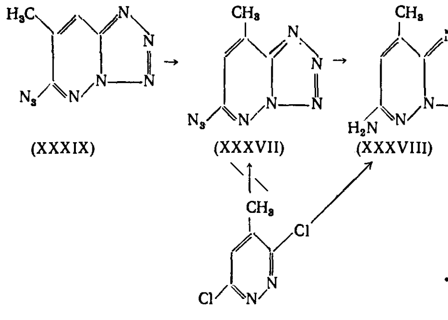


(XXXV)

(a) $R_1=R_2=H$; (b) $R_1=CH_3$, $R_2=H$; (c) $R_1=C_6H_5$, $R_2=H$;
(d) $R_1=H$, $R_2=CH_3$; (e) $R_1=H$, $R_2=C_6H_5$.

It has been shown that, when 3,6-dichloro-4-methylpyridazine (XXXVI) is treated with sodium azide in ethylene glycol, the 8-amino-derivative (XXXVIII) is formed as a result of the reduction of the azido-group instead of the expected 6-azido-8-methyltetrazolo[1,5-*b*]pyridazine

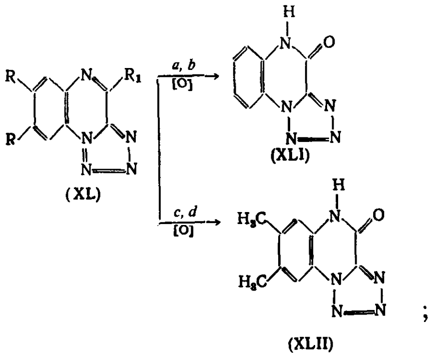
(XXXVII).[91] When 6-azido-7-methyltetrazolo[1,5-*b*]pyridazine (XXXIX) is heated in ethylcellosolve, it isomerises with subsequent reduction to the amino-derivative (XXXVIII):



5. Oxidation

Like 1,5-disubstituted tetrazoles, the condensed tetrazole ring sometimes exhibits an appreciable resistance to oxidation. Thus the oxidation of quinolino[1,2-*e*]tetrazole with a solution of potassium permanganate leads to the formation of tetrazole and the quantitative evolution of carbon dioxide[54]. Tetrazolo[1,5-*a*][1,8]-naphthyridines behave similarly[29,39].

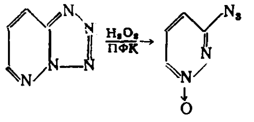
Postovskii and coworkers[11] studied the action of various oxidants on tetrazolo[1,5-*a*]quinoxalines (XL), which resulted in the isolation of the tetrazolo[1,5-*a*]quinoxalinones (XLI) and (XLII):



(a) $R=R_1=H$; (b) $R=H$, $R_1=CH_3$; (c) $R=CH_3$, $R_1=H$; (d) $R=R_1=CH_3$.

Oxidants decompose the tetrazole ring when the ring carbon atom carries a nitrogen-containing substituent. For example tetrahydrotetrazolo[1,5-*a*]quinazoline is oxidised by potassium permanganate to adipic acid and ammonia[99]. When 6-methyltetrazolo[1,5-*b*]benzothiazole and 9-methyl-5-phenyltetrazolo[1,5-*c*]quinazoline react with aqueous solutions of potassium permanganate, the methyl group is oxidised to the carbonyl group[67,93].

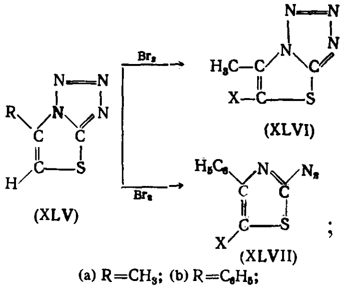
Treatment of tetrazolo[1,5-*b*]pyridazine (XLIII) with hydrogen peroxide in polyphosphoric acid leads to the simultaneous *N*-oxidation and opening of the tetrazole ring with formation of 3-azidopyridazine N-oxide (XLIV)[57]:



6. Electrophilic Substitution Reactions

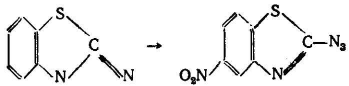
The structure of the products of electrophilic substitution reactions involving condensed tetrazoles depends in many respects on the stability of the tetrazole ring and on the electronic nature of the substituent introduced into the nitrogen-containing heterocycle. Powerful electron-accepting substituents or substituents with a negative inductive effect destabilise the condensed tetrazole ring and promote the formation of reaction products having the azide structure.

It has been shown that bromination and the introduction of thiocyanato-groups into 6-methylthiazolo[2,3-*e*]tetrazole (XLVa) take place in the 5-position of the condensed system with formation of the corresponding 5-bromo- and 5-thiocyanato-derivatives (XLVI). The reactions with the 6-phenyl-substituted derivative (XLVb) proceed similarly in the 5-position, but, owing to the lower stability of the tetrazole ring, the isomeric azido-derivatives (XLVII) are formed in this case[84,100]:



(a) $R=CH_3$; (b) $R=C_6H_5$; X=Br, CNS.

The sulphonation, chlorosulphonation, and nitration reactions of compound (XLVb) also involve the 5-position. The introduction of strong electron-accepting substituents promotes the opening of the tetrazole ring at the $N_{(1)}-N_{(2)}$ bond with formation of the isomeric 2-azido-derivatives[66,84]. Tetrazolo[5,1-*b*]benzothiazole is nitrated in the 7-position of the condensed system and the nitration product has the structure of 2-azido-5-nitrobenzothiazole (XLVIII):

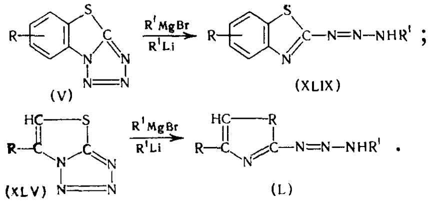


It has been observed[84] that the tetrazole ring is protonated in electrophilic substitution reactions carried out in the presence of inorganic acids and the tetrazolium salt reacts. In a concentrated acid, the reaction product retains the structure of the tetrazolium salt. When the reaction mixture is diluted with water, the salt is hydrolysed and the condensed tetrazole isomerises to the 2-azido-derivative in consequence of the introduction of an electron-accepting substituent into the thiazole or benzothiazole ring.

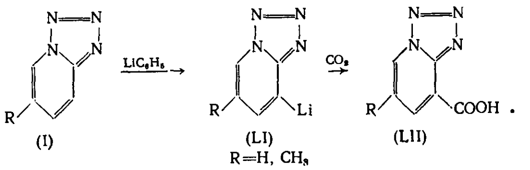
Sasaki et al.[86] showed that tetrazolo[5,1-*a*]pyridine (I) is nitrated and brominated in the 6-position with formation of the 6-nitro- and 6-bromo-derivatives.

7. Reactions with Organometallic Compounds and Sodium Cyanide

It has been shown for derivatives of tetrazolo[5,1-*b*]benzothiazole (V) and thiazolo[2,3-*e*]tetrazole (XLV) that the course of the reactions with organomagnesium bromide and organolithium derivatives depends on the position of their azide–tetrazole equilibrium and the nature of the organometallic reagent[48,64,101,102]. In contrast to the 4-methyl derivative (V) and the 6-methyl derivative (XLV), which do not react with such organometallic reagents, compound (V) and its 6-methyl, 6-chloro-, 6-methoxy-, and 4-chloro-derivatives as well as the 6-phenyl derivative of compound (XLV) give rise respectively to benzothiazol-2-yl-triazenes (XLIX) and thiazol-2-yltriazenes (L)[48,64,101,102]. It is interesting that compound (V) and its 6-methyl- and 6-chloro-derivatives are converted into triazenes only in reactions with phenylmagnesium bromide and phenyl-lithium:

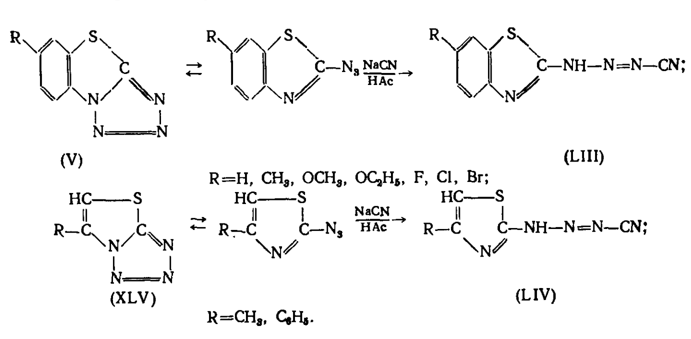


When tetrazolo[5,1-*a*]pyridine (I) and its methyl derivative are treated with phenyl-lithium, the pyridine ring is metallated, while the tetrazole ring remains unchanged. The lithio-derivatives (LI) obtained in this way were then converted into carboxylic acids (LII):



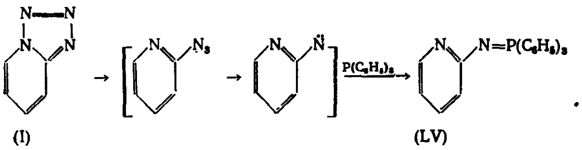
The reaction of the tetrazole ring with organometallic compounds probably requires a definite degree of electron-accepting capacity of the substituents in the condensed tetrazole and of the organic group linked to the metal.

Like aromatic azides, the tetrazoles (V) and (XLV) readily react with sodium cyanide, forming benzothiazol-2-ylcyanotriazenes (LIII) and thiazol-2-ylcyanotriazenes (LIV) respectively[64,102]:

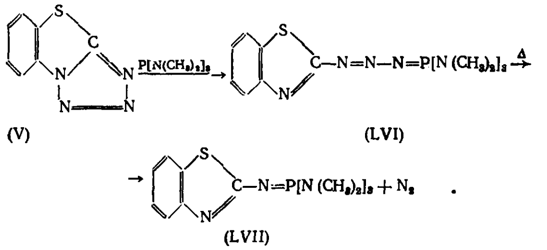


8. Reactions with Organophosphorus Compounds

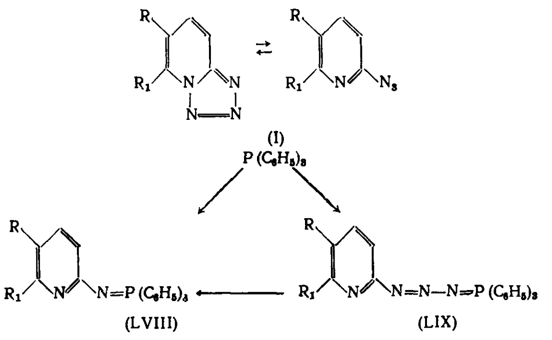
Aromatic azides are known to form aryliminophosphoranes on reaction with triphenylphosphine[103]. The interaction of condensed tetrazoles with triphenylphosphine was described for the first time by Sasaki and Kanematsu[107] with tetrazole (I) as an example. It is believed that under the reaction conditions the tetrazole isomerises to the azido-derivative, which is followed by a thermally induced loss of nitrogen and the interaction of 2-pyridylnitrene with triphenylphosphine, the product being 2-triphenylphosphazopyridine (LV):



Zhmurova et al.[105] studied this reaction with certain tetrazolo[5,1-*b*]benzothiazoles (V) and thiazolo[2,3-*e*]-tetrazoles (XLV). Since the reaction proceeds under mild conditions (in benzene at 50–60°C), the formation of benzothiazol-2-yl- and thiazol-2-yl- nitrenes as intermediates is doubtful. The authors suggested that the reaction of these tetrazoles with triphenylphosphine is due to the presence in the solution of azido-forms and that it involves the usual oxidative imination of tertiary phosphines by organic azides. This hypothesis was confirmed indirectly by the isolation of the intermediate phosphazide (LXI) in the reaction of compound (V) and phosphorous hexamethyltriamide. The phosphazide subsequently decomposes with formation of the phosphazo-compound (LVII):

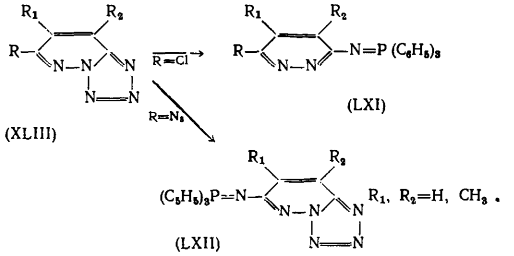


Sasaki et al.[106] investigated the interaction of compound (I) and some of its derivatives with triphenylphosphine in various solvents and at different temperatures. They showed that the reaction is of second order and that its rate and mechanism depend on the electronic nature of the ring substituents, on the type of solvent, and temperature. Thus, substituents promoting ring opening and the formation of the isomeric azido-form accelerate the formation of the iminophosphoranes (LVIII) via the intermediate triazenophosphoranes (LIX). A decrease of solvent polarity and an increase of reaction temperature act in the same direction.



In the absence of the reactive azido-form from the solution, the reaction involves the $N_{(1)}$ or $N_{(3)}$ atoms of the tetrazole ring, after which the ring is cleaves with subsequent loss of nitrogen and the formation of compound (LVIII).

Tetrazolodiazines[107], i.e. tetrazolo[1,5-*b*]pyridazine (XLIII) and tetrazolo[1,5-*a*]pyrazine (LX) and their derivatives, also form iminophosphoranes on reaction with triphenylphosphine. Electron-accepting substituents in the pyridazine and pyrazine rings facilitate this reaction, while electron-donating substituents stabilise the tetrazole ring and preclude the reaction:



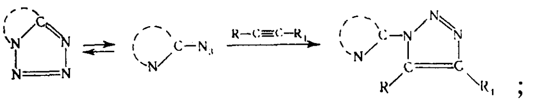
(XLIII) (LXI) (LXII)

Thus, the unsubstituted compound (XLIII) and its 5-methoxy-derivative do not interact with triphenylphosphine even on refluxing in chlorobenzene, while the 5-chloro-derivatives form the corresponding iminophosphoranes.

The 5-azido-derivative (XLIII) reacts with an excess of triphenylphosphine only via the azido-group, forming monoiminophosphoranes (LXII). Evidently, the iminophosphorane group formed behaves as an electron-donating substituent and stabilises the tetrazole ring. The reaction mechanism depends on the position of the azide–tetrazole equilibrium in solution also in the case of tetrazolopolyazines. If only the tetrazole forms (XLIII, R = Cl) and (LX) are present, the $N_{(1)}$ and $N_{(3)}$ atoms of the tetrazole ring are subjected to nucleophilic attack by triphenylphosphine. If only the azido-isomer of the 5,6-diphenyl derivative of compound (LX) is present in acetic acid under the reaction conditions, the reaction involves the formation of triazenophosphorane. When both tautomeric forms of compound (LX) are present in the reaction mixture in chloroform, the reaction proceeds in both ways.

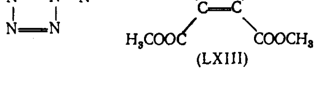
9. Cycloaddition Reactions and Others

It has been shown that tetrazolo[5,1-*a*]pyridine (I)[108] and its 5-chloro-, 6-bromo-, and 6-nitro-derivatives[86], 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine[108], and 7,8-diphenyltetrazolo[1,5-*a*]pyrazine[26] undergo cycloaddition reactions with propiolate and acetylenedicarboxylate esters and diphenylacetylene, forming the corresponding substituted triazoles:



R = H, R₁ = COOCH₃; R = R₁ = COOCH₃; R = R₁ = C₆H₅ .

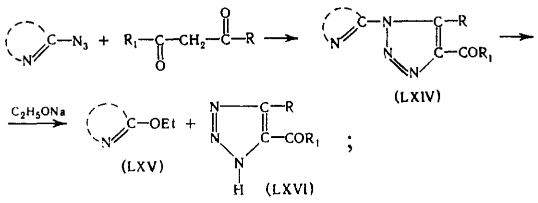
All these reactions proceed via the preliminary isomerisation to the azido-form and the yield of the triazole under the reaction conditions depends on the rate of isomerisation. It has been noted[26] that even in boiling toluene 6-azidotetrazolo[1,5-*b*]pyridazine reacts with dimethyl acetylenedicarboxylate only via the azido-group, forming the product (LXIII):



(LXIII)

while the tetrazole ring does not react. On the other hand, 7,8-diphenyltetrazolo[1,5-*a*]pyrazine takes part in this reaction at a temperature as low as 62°C in chloroform, which indicates a greater tendency of the tetrazole ring towards isomerisation in the latter compound.

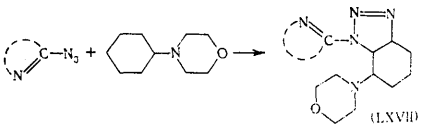
Triazoles are not always the final products of such reactions. Several instances have been described where cycloaddition with formation of triazoles is an intermediate stage. Under the reaction conditions, the triazoles may be cleaved, which leads to the formation of secondary reaction products. Thus it has been reported[109] that the interaction of tetrazolo[5,1-*b*]benzothiazole and tetrazolo[1,5-*b*]1,2,4-triazine with compounds of the type $R-\overset{\overset{O}{\|}}{C}-CH_2-COR$ (where R = CH_3 or C_6H_5) proceeds with formation of the corresponding cycloaddition products (LXIV), which are relatively unstable under the reaction conditions and are cleaved at the C–N bond between the heterocyclic rings with formation of 2-ethoxy-derivatives of the corresponding heterocycles (LXV) and substituted triazoles (LXVI):



R = CH₃, R₁ = C₆H₅; R = R₁ = CH₃ .

When the same tetrazoles react with ethylbenzoyl acetate, the stable sodium salt of the corresponding cycloaddition product may be isolated; on acidification with hydrochloric acid, the sodium salt is hydrolysed with evolution of nitrogen and carbon dioxide and formation of 2-aminobenzothiazole and ω-chloroacetophenone.

Fusco et al.[110] found that, like azides, condensed tetrazoles react with *N*-(α-cyclohexenyl)morpholine, also forming 1,2,3-triazole derivatives (LXVII):

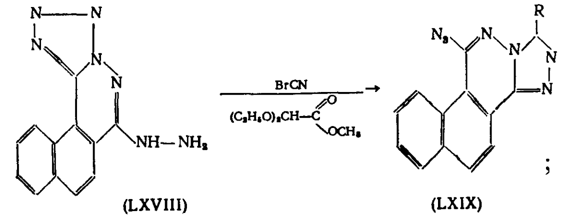


(LXVII)

The cycloaddition of 4,5-dimethyltetrazolo[1,5-*a*]pyrimidine and tetrazolo[5,1-*a*]pyridine to norbornene proceeds in a similar manner[108]. The interactions of these tetrazoles with cyclohexene, 1,2-dihydronaphthalene, indene, *trans*-stilbene, 1,1-diphenylethylene, and dimethyl maleate and fumarate have been investigated[108] and it has been found that the cycloaddition products are the corresponding triazoles, which are cleaved under the reaction conditions with subsequent formation of enamines and the evolution of nitrogen.

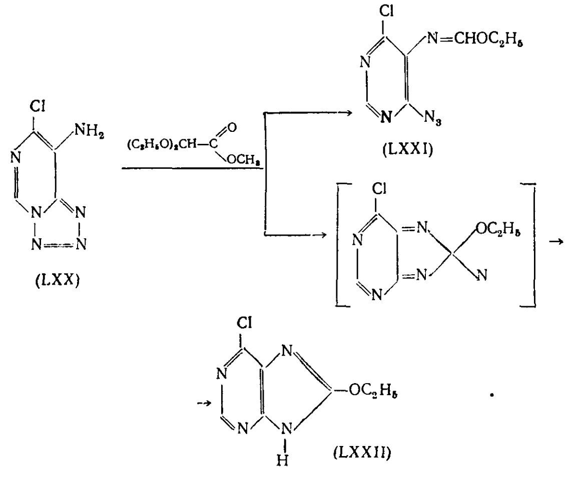
Stanovnik and Tišler[20,21] studied the interaction of 6-hydrazino-7,8-dihydrobenzo[*h*]tetrazolo[5,1-*a*]phthalazine (LXVIII) with diethoxymethyl acetate or bromocyanogen and found that this involves the destabilisation and opening of the tetrazole ring with formation of the azido-derivative. As a result, a new condensed triazole ring

(LXIX) is formed, destabilising the tetrazole ring and converting it into the azido-form:

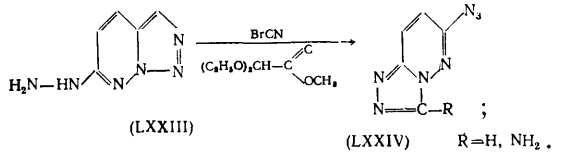


(LXVIII) (LXIX) R=H, NH₂ .

The interaction of diethoxymethyl acetate with 8-amino-7-chloro-tetrazolo[1,5-*c*]pyrimidine (LXX) at room temperature, leading to the formation of the corresponding ethoxymethylene derivative (LXXI), has been described[111]. The tetrazole ring is ruptured in this process. On heating in anisole, 6-chloro-8-ethoxypurine (LXXII) is formed:



The attempts to obtain a tricyclic derivative by treating 6-hydrazinotetrazolo[1,5-*b*]pyridazine (LXXIII) with diethoxymethyl acetate or bromocyanogen led to the opening of the tetrazole ring and the formation of 3-R-6-azido-*s*-triazolo[4,3-*b*]pyridazine (LXXIV)[20,21]:



(LXXIII) (LXXIV) R=H, NH₂ .

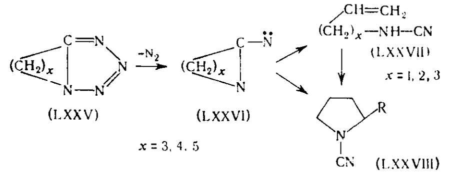
10. Thermolysis and Photolysis

Many condensed tetrazoles are known to be converted into the isomeric azido-derivatives even at room temperature or on slight heating. Therefore it was to be expected that even condensed tetrazoles which do not exhibit a tendency towards the azide–tetrazole tautomerism might be converted into azides at high temperatures and might undergo thermal decomposition of the azide type.

The behaviour of condensed tetrazoles on heating has been investigated for polymethylenetetrazoles[112], tetrazolo[5,1-*a*]pyridine[51,52,86,88,113-117], tetrazolo[5,1-*a*]quinoline[60], tetrazolo[1,5-*a*]pyrimidine[113,118-120], tetrazolo[1,5-*c*]pyrimidine[119], tetrazolo[1,5-*a*]quinoxaline[60], tetrazolo[1,5-*a*]pyrazine[26,119], tetrazolo[1,5-*a*]pyridazine[26,53,119,121], tetrazolophenanthridine[60], tetrazolo[1,5-*c*]quinazoline[60], and certain others.

The reactions were carried out in the gas phase or in solvents, sometimes using copper acetylacetonate as the catalyst, which made it possible to reduce the thermolysis temperature (evolution of nitrogen) by approximately 100°C. In all the cases investigated the first stage of the thermolysis is the cleavage of the condensed tetrazole ring at the $N_{(1)}-N_{(5)}$ bond and the formation of the isomeric α-azido-derivative. The azide formed then loses nitrogen and gives rise to a nitrene radical, which is subsequently stabilised via several mechanisms, depending on the reaction conditions (solvent, temperature).

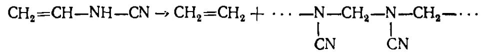
One important pathway to the stabilisation of the nitrene is its conversion into the corresponding α-amino-derivative as a result of the abstraction of hydrogen from the solvent and the formation of secondary amines as well (reaction with a neighbouring reactive group). Nitrenes can also undergo cycloaddition reactions with aromatic hydrocarbons, stilbenes, and nitriles. The cleavage of the ring and the formation of various unsaturated cyano-compounds or their polymerisation products are also possible (particularly at high temperatures in the gas phase). Ring contraction and the formation of various nitrogen-containing heterocyclic cyano-derivatives containing one carbon atom less frequently take place in the gas phase. It has been suggested that the latter process proceeds via the formation of ring cleavage products as intermediates with participation of nitrene nitrogen[115] or via the formation of bicyclic systems. Dimers are sometimes formed[60]. Thus polymethylenetetrazoles (LXXV), which do not exhibit a tendency towards isomerisation, under thermal decomposition in the gas phase at 450–675°C with formation of the nitrene (LXXVI), which then recombines with formation of alkenylcyanamides (LXXVII) (on ring opening) and 1-cyanopyrrolidine (LXXVIII) or its alkyl derivatives (on ring contraction[112]):



(LXXV) (LXXVI) (LXXVIII)

x = 3, 4, 5

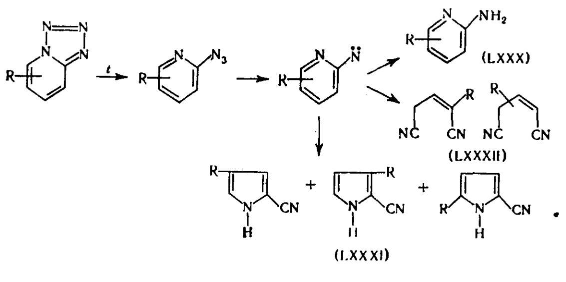
In the reaction involving trimethylenetetrazole, the propenylcyanamide formed evolves nitrogen and gives rise to poly-*N*-cyanoformamidine (LXXIX):



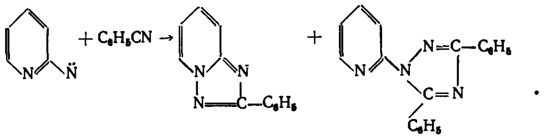
$$CH_2{=}CH{-}NH{-}CN \rightarrow CH_2{=}CH_2 + \cdots -\underset{CN}{\underset{|}{N}}-CH_2-\underset{CN}{\underset{|}{N}}-CH_2-\cdots$$

(LXXIX)

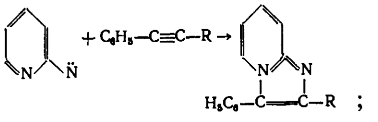
It is known that tetrazolo[5,1-*a*]pyridine (I) is not converted into the isomeric 2-azidopyridine even on heating to 120°C. However, under more severe conditions in the gas phase or in the presence of a catalyst, isomerisation does take place with formation of 2-pyridylnitrene accompanied by the evolution of nitrogen. The process also involves the formation of 2-aminopyridine (LXXX), 2-cyanopyrroles (LXXXI) on ring contraction, and the nitrile of glutaconic acid (LXXXII) on ring opening[26,113,117,118]. It has been shown[115-117] that 2-pyridylnitrene is converted into 2,7-diazatropylidene in the gas phase with ring expansion, the product being subsequently converted into a cyanoazole following ring contraction. In the presence of a catalyst (copper acetylacetonate), there is no ring expansion with formation of diazepines:



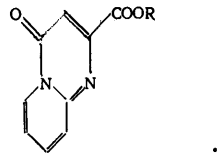
The thermolysis of tetrazolo[5,1-*a*]pyridine and its 6-bromo-, 6-nitro-, 8-nitro-, and 8-bromo-derivatives in solvents without a catalyst or in the presence of copper acetylacetonate[51,52,86,113] is accompanied by the interaction of 2-pyridylnitrene with solvents. In these cases the pyridine ring is preserved. The structure of the reaction products depends on the type of solvent. Thus, when the reaction is carried out in cyclohexane, cyclohexene[113], and toluene[86] in the presence of copper acetylacetonate, the main reaction product is 2-aminopyridine. In benzonitrile [3 + 2] cycloaddition takes place and 2-phenyl-3-triazolo[1,5-*a*]pyridine (LXXXIII) is formed with 2-(3,5-diphenyl-1,2,4-triazolyl)pyridine (LXXXIV) as an admixture[113]:


(LXXXIII) (LXXXIV)

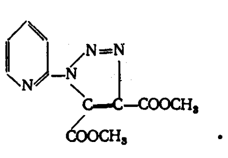
Thermolysis in the presence of dienophiles (ethyl phenylpropiolate, diphenylacetylene) involves 3 + 2 cycloaddition of alkynes with formation of imidazopyridine derivatives (LXXXV):


(LXXXV)

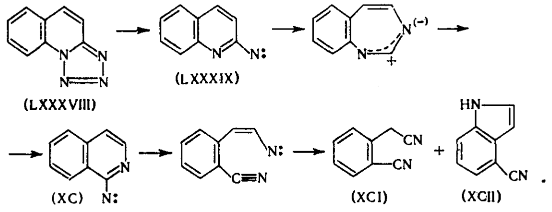
$R=C_6H_5$, $COOC_2H_5$;


(LXXXVI)

Cycloaddition to fumaric acid[114] proceeds with formation of the analogous product (LXXXVI). However, in the presence of dimethyl acetylenedicarboxylate, compound (LXXXVII) is formed[86]:


(LXXXVII)

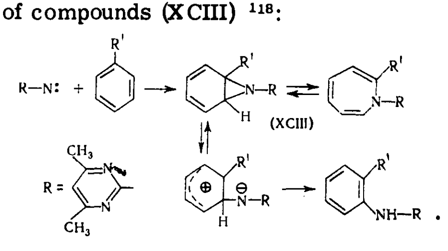
It has been shown[60] that the 2-quinolinylnitrene (LXXXIX) formed in the gas-phase thermolysis of tetrazolo[5,1-*a*]quinoline (LXXXVIII) is converted into 1-isoquinolinylnitrene (XC), possibly via preliminary ring expansion to azatropylidene followed by ring opening and the formation of compounds (XCI) and (XCII):



The thermolysis of tetrazolo[5,1-*a*]isoquinoline proceeds similarly[60].

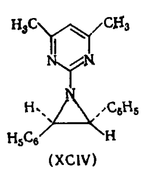
The thermolysis of tetrazolo[1,5-*a*]pyrimidine and tetrazolo[1,5-*c*]pyrimidine in the gas phase also involves isomerisation to the azido-derivatives, the loss of nitrogen, and the formation of pyrimidin-2-yl- and pyrimidin-4-yl-nitrenes. Subsequently pyrimidin-2-ylnitrene and its derivatives are converted via ring contraction into 1-cyano-3-R-5-R′-pyrazoles and 2-amino-4-R-6-R′-pyrimidines[119]. The 1-cyanopyrazoles formed can split off HCN with formation of pyrazoles (at 500°C), while under more severe conditions (at 700°C) nitrogen is split off with formation of cyanopenta-2,4-dienes[120]. Under still more severe conditions, the unsubstituted 3*H*-pyrazole gives rise to cyanoallene and tetrolonitrile in proportions of 1 : 3.

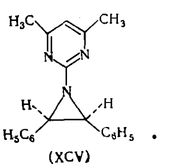
On gas-phase pyrolysis, tetrazolo[1,5-*c*]pyrimidine gives rise to cyanoimidazoles only[119]. The pyrolysis of tetrazolo[1,5-*a*]pyrimidines in solvents (cyclohexane, isobutane, naphthalene, anthracene, phenanthrene, mesitylene, and anisole[118,122]) involves the formation of 2-aminopyrimidine, secondary 2-aminopyrimidines, or a mixture of both. Furthermore, pyrimidin-2-ylnitrene can take part in cycloaddition reactions with aromatic hydrocarbons via the following mechanism involving the formation of compounds (XCIII)[118]:



7-Methyl-5-methylthiotetrazolo[1,5-*c*]pyrimidine gives rise to 1-cyano-4-methyl-2-methylthioimidazole on pyrolysis in organic solvents, i.e. ring contraction can occur also in solvents; in addition, amino-derivatives are produced[122].

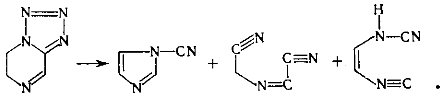
The pyrolysis of tetrazolo[1,5-*a*]pyrimidines in the presence of *trans*-stilbene without a catalyst (160°C) or in the presence of a catalyst (copper acetylacetonate, 120°C), leading to the formation of derivatives of *trans*- and *cis*-aziridines (XCIV) and (XCV) (40% and 3% respectively) has also been described[113]:


(XCIV)


(XCV)

The pyrolysis of 8-phenyltetrazolo[1,5-*c*]pyrimidine in dichlorobenzene[123] proceeds with formation of indole in 50% yield. When the above tetrazole was refluxed in trifluoroacetic acid, mainly the initial product, which failed to react, was isolated. On gas-phase pyrolysis, tetrazolo[1,5-*a*]quinoxaline and tetrazolo[5,1-*c*]quinazoline form identical products. Ring contraction results in the formation of 2-cyanobenzimidazole and ring opening gives rise to *N*-cyanoanthranilonitrile[60].

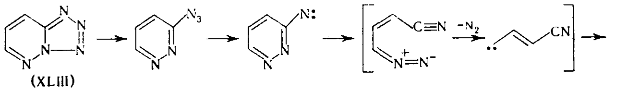
The pyrolysis of tetrazolo[1,5-*a*]pyrazine (XCVI) in the gas phase[19,122] involves ring contraction and the formation of compound (XCVII) and the ring cleavage products (XCVIII) and (XCIX):



(XCVI) (XCVII) (XCVIII) (XCIX)

In organic solvents (cyclohexane) the thermolysis proceeds with formation of 2-aminopyrazine[122], which confirms the formation of a nitrene and 1-cyanoimidazole as a result of ring contraction. On heating in acetic acid, the 5,6-diphenyl derivative of compound (XCVI)[8] gives rise to a mixture of 2,5-diphenylimidazole (56%) and 1-acetyl-5-diphenylimidazole (3%). Wentrup's studies[122] have shown that the formation of these products can be readily accounted for by the primary contraction of the nitrene ring.

In the thermolysis of tetrazolo[1,5-*b*]pyridazine (XLIII)[119], one of the most stable of the condensed tetrazoles, ring opening results in the formation of cyanoallene (C), tetrolonitrile (CI), propargyl cyanide (CII), and 2-cyanocyclopropene (CIII):

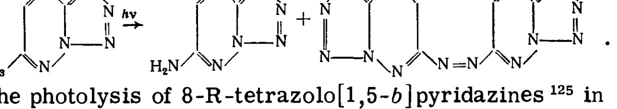


(XLIII)

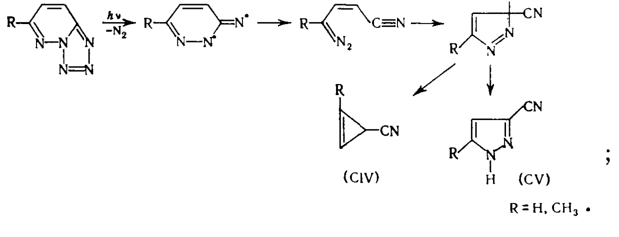
(C) (CI) (CII) (CIII)

When 9,10-tetrazolophenanthridine is heated to 500°C, a nitrene dimer is formed and then 9-cyanocarbazole and 4-cyanocarbazole (possibly as a result of ring opening and recyclisation[60]).

The photolysis of 6-azidotetrazolo[1,5-*b*]pyridazine in alcoholic solution for 20 h leads to the formation of a mixture consisting of 95% of 6-aminotetrazolo[1,5-*b*]pyridazine, 3% of the corresponding azo-compound, and 2% of a polymer[124]:



The photolysis of 8-R-tetrazolo[1,5-*b*]pyridazines[125] in methanol or methylene chloride results mainly in the formation of 3-cyano-R-cyclopropenes (CIV) in 20–25% yield and 3-cyano-5-R-pyrazoles (CV) in 0.1% yield. In acetone the yield of compounds (CIV) decreases to 5%, while compounds (CV) are not formed:

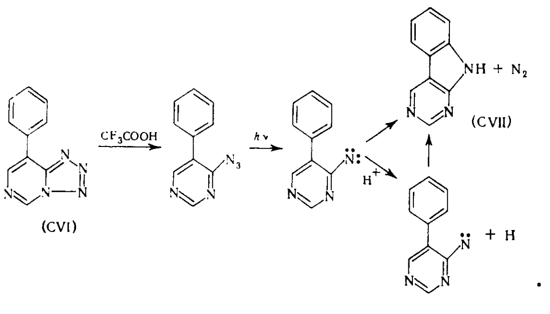


(CIV) (CV)

R = H, CH$_3$.

7,8-Diphenyltetrazolo[1,5-*a*]pyrazine decomposes photolytically in acetic acid in the course of 32 h with formation of 4,5-diphenylimidazole (10%) and benzoic acid (7%).[26]

The photolysis of 8-phenyl-, 8-*p*-tolyl-, 8-*p*-methoxyphenyl-, and 8-*p*-chlorophenyl-tetrazolo[1,5-*c*]pyrimidines (CVI) in trifluoroacetic acid leads to the corresponding 2*H*-pyrimido[4,5-*b*]indoles (CVII)[123], which are formed in a high yield. This process can be used as a method for the synthesis of indoles. In a non-polar medium, photolysis takes place slowly and with low yields. The quantum yield of the photolysis of the 8-phenyl derivative is 0.5:



(CVI) (CVII)

o0o

The properties of condensed tetrazoles, the mode of various reactions in which they are involved, and the structures of the reaction products are directly related to the distribution of electron density in the molecule. The latter is in turn determined by the electron-accepting properties of the tetrazole ring and of the nitrogen-containing heterocycle and by the electronic nature of the substituents.

The distribution of electron density influences the stability of the condensed tetrazole ring and its capacity for being opened at the $N_{(1)}$–$C_{(5)}$ bond with formation of the isomeric azidoazomethine derivatives of the nitrogen-containing heterocycles. The protonation, alkylation, electrophilic substitution, covalent hydration, and reduction reactions as well as reactions with alkalis depend on the electron-accepting properties of the tetrazole ring.

The stability of the tetrazole ring determines the mode and rates of reactions with nucleophilic agents, cycloaddition reactions, thermolysis, photolysis, and reactions with organometallic, organophophorus, and other compounds.

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Present State of the Theory of Homogeneous Nucleation

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The present state of the theory of the spontaneous condensation of a supersaturated vapour is discussed, and modern methods for calculating the free energy of nuclei of the new phase are examined, especially in the light of the resolution of the Lothe-Pound paradox. Reasons for the differences between the best known formulae for the rate of nucleation ara analysed. The limits of applicability of the existing theory to practical calculations are deduced from a consideration of a large quantity of experimental data, and specific problems that have not yet been completely solved are mentioned. A list of 179 references is included.

CONTENTS

I. INTRODUCTION

Many theoretical and experimental studies have been made on nucleation in a supersaturated vapour, both because of the fundamental importance of the kinetics of phase transitions of the first kind and because of the need to establish methods for engineering calculations on bulk condensation, which are required in many branches of technology. During recent years considerable progress has been made in this direction. In the theory of nucleation inaccuracy has been revealed in the Lothe–Pound concept, new methods have been established for calculating the bonding energy of small nuclei, and the mathematics of the theory has been improved significantly. New methods have appeared for studying nucleation–molecular beams, improved diffusion cells, and apparatus for investigating condensation during turbulent mixing—and laser techniques have been widely employed for tracing the growth of the disperse phase. Condensation from the vapour has been studied on a greater range of substances. New methods for calculating bulk condensation have been developed. The present Review summarises and analyses these achievements.

II. KINETICS OF FORMATION OF A NEW PHASE IN A SUPERSATURATED VAPOUR—GENERAL APPROACH

Almost all current theories of the formation of a new phase from a supersaturated vapour are based on the so called Szillard model, according to which a supersaturated vapour comprises a mixture of monomeric molecules and molecular aggregates (clusters) containing different numbers of molecules. Clusters are able either to vaporise or to grow by adding molecules and finer clusters. The mathematical description of this model is based on the so called quasi-chemical approximation, which regards clusters of each size as chemical compounds characterised by definite free energies of formation from the monomer. Such an approach is rather unsound logically since, as will be shown later, calculation of the free energies of formation of clusters requires that the partition function of the system shall be expressed as a combination of small partition functions written for clusters of each size. Yet statistical thermodynamics should describe a system in a state of true—not metastable—equilibrium, and its application to a system whose parameters of state represent a region lying between the binoidal and the spinodal should give Maxwell's phase rule, as was demonstrated by Kac et al.[1] The statistical-mechanical formulation in current nucleation theory is therefore largely arbitrary and approximate, with the closeness of its approximation diminishing as the system moves from the binoidal towards the spinodal.

The purpose of nucleation theory is to preduct the rate I of formation of stable particles of the condensed phase per unit volume of the supersaturated vapour under given external conditions, and also to determine the size at which these particles become stable. The free energy of formation of clusters ΔG_g increases with size for very small clusters, then passes through a maximum, and decreases to negative values. Clusters of size corresponding to the maximum free energy are said to be "critical", and are equally likely to grow or to vaporise. Nuclei characterised by negative free energies are completely unstable and capable only of growth. Such a system, corresponding to the Szillard–Farkas scheme, can be described by an infinite series of differential equations:

$$\frac{\mathrm{d}f_g}{\mathrm{d}t}=\frac{1}{2}\sum_{k=1}^{g-1}\beta_{g-k,k}f_{g-k}f_k+\sum_{k=g+1}^{\infty}\alpha_{k-g}^{k}f_k-f_g\left(\sum_{k=1}^{\infty}\beta_{gk}f_k+\frac{1}{2}\sum_{k=1}^{g-1}\alpha_{g-k,k}^{g}\right), \quad (1)$$

where f_g is the concentration of clusters comprising g molecules, β_{ij} is the probability of formation of a cluster of size g by the collision of i and j molecules, and α_{ij}^{g} is the probability that a cluster of size g will break down into clusters of sizes i and j.

It is useful for the subsequent discussion to distinguish two extreme cases of nucleation, which, following Gerlach[2], we shall term "rapid" and "slow" nucleation. Contemporary literature refers more often to condensation at high and at low supersaturations of the vapour S, but this seems less appropriate, since it is difficult to choose a criterion for assessing supersaturation. The absolute supersaturation means nothing by itself, since for different substances and under different conditions the same supersaturation may correspond to rates of nucleation, i.e. rates of formation I of nuclei of supercritical size, differing by several powers of ten. Nor can the critical supersaturation S_{cr}, corresponding to $I = 1$, be regarded as significant, since it may vary over a similarly wide range as the temperature changes from the absolute zero to the critical point, with the character of nucleation at a constant rate I also varying with temperature. It is advisable to use the degree of reversibility of migration of a cluster along the size (g) axis as a measure of the rapidity of condensation. White showed[3] that under steady-state conditions the mean time required for a cluster to pass from the point $g = 1$ into the supercritical region is f_1/I. A dimensionless parameter for the rapidity of nucleation can be obtained by dividing this quantity by the time of collision between molecules of the vapour at zero time $\beta_1 f_1^0$. The resulting parameter $\theta^* = f_1^2\beta_1 I^{-1}$ has values of 10^{22}–10^{28} for the condensation of water or alcohol vapour in Wilson cloud chambers (typical cases of slow nucleation) and only 10^3–10^4 for the condensation of the highly dilute vapours of inorganic substances.

Rapid condensation is characterised by small (<10) critical nuclei, a sharp decrease in the free energy of formation of clusters in the supercritical region (so that the addition of one molecule to a critical cluster is equivalent to falling into a trap), and a considerable role of collisions between clusters. In slow condensation the critical nucleus contains several tens of molecules, and clusters grow by adding single molecules of the monomer (provided that the vapour is not already associated in the unsaturated state). It is significant also that processes of the rapid type overlap in time with the coagulation of supercritical particles, whereas slow processes are separated in time from subsequent coagulation. Slow nucleation usually occurs in relatively dense vapours (and partial pressures >0.1 mmHg), but rapid nucleation at low vapour densities, since in the latter case condensation during supersaturation is unable to diminish its extent significantly. Difficulties are involved in describing both types of processes. Thus with rapid nucleation the free energy ΔG_g cannot be expressed in terms of parameters of macroscopic quantities of the condensed phase, since such processes are usually accompanied by change in the external conditions. Slow nucleation takes place at a temperature comparable with the critical point, leading to thickening of the interfacial layer on the nuclei and making it difficult to describe their properties. The concentration ratio of the carrier gas to the vapour is far greater in rapid than in slow nucleation, which ensures the isothermal character of the process and the relaxation of the distribution of energy between degrees of freedom of the cluster in the time intervals between successive collisions between it and molecules of the vapour.

The greatest attention has hitherto been paid to slow nucleation in a monomolecular vapour with the concentration of the monomer maintained constant. A considerable number (>30) of formulae have been suggested for the rate I under steady-state conditions, which makes it difficult to choose an expression for the analysis of experimental results or for engineering calculations. We shall therefore repeat the deduction of the formula for the rate of nucleation, incidentally mentioning the sources of discrepancies between the results of different authors and examining individual attempts to improve the theory.

The migration of nuclei along the size axis, caused by the addition or the evaporation only of individual molecules, is described by the equation

$$\frac{\mathrm{d}f_g}{\mathrm{d}t} = I_{g+1} - I_g, \tag{2}$$

where I_{g+1} is the number of nuclei passing in unit time fro from the point g to the point $g + 1$, which can be expressed

$$I_g = \beta_{g-1} f_1 g_{g-1} - \alpha_g f_g. \tag{3}$$

The set of equations (2) in principle enables the distribution $f_g(t)$ to be determined at any time provided that formulae are known for α_g and β_g.

We shall now make certain general statements, whose validity is independent of the specific form of α_g and β_g. Firstly we consider the steady-state process, when f_g is independent of t, so that I is independent of g. We rewrite (3) in the form

$$I = -\alpha_{g-1} f_{g-1} + \beta_g f_g f_1 \tag{5†}$$

which represents a set of inhomogeneous linear equations in f_g. In order to find I, we first solve the homogeneous equation

$$\alpha_{g-1} c_{g-1} - \beta_g f_1 c_g = 0 \tag{6}$$

when we have

$$c_g = \prod_{j=2}^{g-1} \frac{\alpha_{j-1}}{\beta_j}. \tag{7}$$

Supposing that $I \neq 0$, we find $f_g = A_g c_g$, where A_g is determined from (5) by the recurrence relation

$$A_g = -I \sum_{s=2}^{g} (\beta_s f_1 c_s)^{-1}. \tag{8}$$

If we put $g = 2$, we have $A = f_1$, so that

$$f_g = c_g \left[f_1 - I \sum_{s=2}^{g} (\beta_s f_1 c_s)^{-1} \right]. \tag{9}$$

The next problem is to find I, which usually involves the assumption that sufficiently large clusters are removed from the system, i.e. that $f_G = 0$ at some point G. From (5) and (9) we then have

$$I = \left[\sum_{s=1}^{G-1} (f_1 \beta_s c_s)^{-1} \right]^{-1}. \tag{10}$$

Combining (9) and (10) gives

$$f_g = c_g I \sum_{s=g}^{G-1} (f_1 \beta_s c_s)^{-1}. \tag{11}$$

Formulae (10) and (11) relate I and f_g to the coefficients α_g and β_g.

The next step should be to express I and f_g in terms of parameters defining the state of the vapour and the properties of the substance, and to transform the sums occurring in these expressions. This would require that the concentrations c_g, which would be maintained in the vapour in the absence of a flux of nuclei along the g-axis, should be identified with the equilibrium concentrations determined from the condition of equality

$$\mu_g = g\mu_1. \tag{12}$$

of the chemical potentials μ_g of the same quantities of substance included in clusters of different sizes. We again recall that this is strictly valid only for equilibrium association in an unsaturated vapour: the soundness of such identification becomes increasingly dubious with deeper penetration into the region of metastable states. Since μ_g can be written as the sum of the standard chemical potential μ_g^0 and the concentration-dependent term $kT \ln c_g^*$ (where c_g^* is determined by some concentration adopted as standard), c_g can be expressed in terms of f_1 and the Gibbs free energy of formation of the cluster $\Delta G^* = \mu_g^0 - g\mu_1^0$:

$$c_g = f_1 \exp(-\Delta G^*/kT). \tag{13}$$

The Kelvin–Gibbs equation is usually employed to express ΔG^* in terms of the surface tension σ and the density ρ of the condensed phase. Logical difficulties associated with this step will be discussed later. Replacing the summation in formula (10) by integration, we obtain for the rate of nucleation

$$I = \left(\int_0^G \frac{\mathrm{d}g}{f_1 \beta_g c_g} \right)^{-1}, \tag{14}$$

(where G is the size of the clusters for which $f_g = 0$), which can be used for the direct calculation of I.

Frenkel'[4] and Zel'dovich[5] replaced the set of difference equations (3) by the equation of diffusion along the g-axis in order to calculate the rate of nucleation. Becker and Döring[6] resorted to direct replacement of the sum (10) by the integral, using the equation $\alpha_{g^*} = \beta_{g^*}$ instead of (6), which entailed an inaccuracy from disregard of the change in surface area of the particle on the vaporisation from it of one molecule, and led to a result differing from that of Frenkel' and Zel'dovich by a factor of $g^{-2/3}$. As shown both by Barnard[7] and by Petrovskii and Amelin[8], when the correct condition (6) is used, the Becker–Döring procedure gives a result identical with that of Zel'dovich and Fenkel'. It may be mentioned here that the difference between Barnard's[7] and the Becker–Döring results is due to the retention by the former, after replacing the sum $\Sigma g^{-1/3}$ by the integral

$$\int g^{-1/3}\,\mathrm{d}g = \frac{3}{2} g^{2/3} - 1 \tag{15}$$

of unity, which undoubtedly improves the accuracy, since replacing a sum by an integral by itself introduces an inaccuracy of the same order. Indeed, White's deduction[3], based on a consideration of discrete migrations along the g-axis and not involving replacement of summation by integration (or other approximate operations), gives precisely the same numerical values of I as do Frenkel'–Zel'dovich calculations. The final calculated result (for steady-state conditions) can be written

$$I = [f_1 \exp(-\Delta G^*/kT)]\,[f_1 \beta_{g^*}]\,Z, \tag{16}$$

where the three factors in square brackets are the equilibrium concentration of nuclei of critical size c_{g^*}, the rate of condensation of the vapour on the critical nuclei, and the so called Zel'dovich factor, which allows for the fact that the concentrations f_g do not reach the equilibrium values c_g. All three quantities are expressed in terms of phenomenological parameters. For ΔG^* we have

$$\Delta G^* = 4\pi r^{*}\sigma, \tag{17}$$

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† The Russian version contains no Eqn. (4) (Ed. of Translation).

where the radius r^* of a critical nucleus is found from the condition $d\Delta G/dr = 0$:

$$r^* = \frac{2\sigma M}{kT\rho N \ln S}; \ \Delta G^* = \frac{16\pi\sigma^3 M^2}{3\,(kT\rho N)^2 \ln^2 S} \tag{18}$$

in which M is the molecular weight, N Avogadro's number, and S the supersaturation. The rate of growth is found by combining (18) with Knudsen's formula:

$$\beta_{1g}f_1 = \frac{\gamma_g f_1 kT}{(2\pi mkT)^{1/2}} \cdot 4\pi r^{*2}, \tag{19}$$

where γ_g is the condensation coefficient and m the mass of the molecule. Finally, for Z we have

$$Z \equiv (f_g/c_g) = (\Delta G/3kT\pi g^{*2})^{1/2} = \frac{\rho \ln^2 SN}{8\pi M}\left(\frac{kT}{\sigma}\right)^{1/2} \tag{20}$$

from which it follows that $Z \simeq 0.01$. Substituting (18)–(20) in (16) yields the Frenkel'–Zel'dovich formula for the rate of nucleation:

$$I = 9.6 \cdot 10^{25} \frac{\gamma}{S\rho} f_1^2 \left(\frac{2M\sigma}{\pi N}\right)^{1/2} \exp\left[\frac{16\pi}{3}\left(\frac{\sigma}{kT}\right)^3 \left(\frac{M}{\rho \ln S}\right)^3\right]. \tag{21}$$

The same (or very similar) expressions were obtained by independent methods by Gerlach[2], by Deryagin[11,12], and in papers already cited[8,9]. Equation (21) is based on the hypothesis that clusters can be regarded as spherical droplets possessing the macroscopic density and surface tension. Some inaccuracy, slight in the case of slow nucleation, is introduced by the use of Knudsen's formula, while the β_{1g} should be expressed as coefficients of the frequency of collision between gas molecules (since clusters must be regarded as molecules of a Lorentzian gas).

Equation (16) applies also to rapid nucleation when occurring under steady-state conditions, and the expressions for Z obtained from a consideration of discrete migrations along the g-axis are equally applicable to the two types of nucleation. Accurate calculations[9,10] show that Z for rapid nucleation is close to unity and in any case at least 0.5. The difference from unity can safely be neglected because of the relative inaccuracy of the determination of ΔG. However, proof of the validity of the formulae for Z in the case of rapid nucleation is essentially of value merely to illustrate the possibility of a common approach to the description of nucleation, since rapid nucleation is usually accompanied by rapid changes in the temperature and the concentration of the vapour, which makes the use of steady-state solutions impossible. The description of nucleation must then be based on the numerical solution of equations of type (2) by means of an electronic computer[13,14].

It must be noted here that with rapid nucleation the cluster concentrations may differ very markedly from the equilibrium values for the instantaneous temperature and monomer concentration. This may be because for small g the condensation coefficient may be strongly dependent on the cluster size and change significantly when g decreases even by unity. According to Gerlach[2] it is sufficient that

$$(\Delta G_{g^*} - \Delta G_{g^*-1}))/kT > 3 \tag{22}$$

in order that Z should be close to unity (disregarding the dependence of γ on g). This condition (22) becomes insufficient when $\gamma(g-1) \ll \gamma(g)$. However, another simplification is possible in this case: with $Z \ll 1$ the possibility of the vaporisation of molecules from the clusters can be neglected, which removes the necessity of solving the complicated problem of determining the free energies of small clusters.

The Reviewers' numerical calculations on rapid condensation[15,16] showed that, after some time θ^* ($\sim 10^3$ in $\beta_1 f_1^0$ units), the monomer becomes completely exhausted, and the subsequent course of the size distribution of condensed particles is governed by coagulation. An asymptotic regime is established, in which the particle concentration decreases with time according to a $t^{-6/5}$ law, as was predicted by Lai et al.[17], and also by Lushinkov[18] for purely coagulation processes (i.e. for systems in which every collision of monomeric particles results in their association with 100% probability).

The quantity θ^* depends on the type of relation between γ and g or on the free energy of formation of the clusters, but never exceeds 10^4 for rapid condensation: independently of its value, the subsequent evolution of the coagulating system follows the same $t^{-6/5}$ variation, with the mean particle size depending unambiguously on the dimensionless time

$$\theta = \beta_{11} f_1^0 t. \tag{23}$$

If the temperature of the system and the concentration by weight of the vapour vary, this quantity is given by[19]

$$\theta = \beta_1 f_1^0 \int_0^t F(t')\, T^*(t')\, dt', \tag{24}$$

where

$$F(t') = \Sigma g f_g / f_1^0$$

is the time variation of the concentration of the condensing substance and

$$T^*(t') = \sqrt{T(t')/T_0};\ T_0$$

in which T_0 is the temperature at zero time. Knowledge of θ permits immediate determination of the number concentration, the preceding particle size, and the size distribution[17-19].

Ultimately, of course, the existence of any gas-disperse system always ends in coagulation, but with slow nucleation the quantity θ^* usually exceeds greatly the lifetime of the system.

III. GROWTH AND VAPORISATION OF CLUSTERS

Following the ideas of Gibbs, the classic theory of nucleation assumes that the free energy of formation of a cluster can be written

$$\Delta G = 4\pi r^2\sigma - kT \ln S = ag^{2/3} - (\mu_v - \mu_l)\, g, \tag{25}$$

where μ_v and μ_l are the chemical potentials of the vapour and of the condensed phase. The second term in (25) can be expressed in terms of σ by means of the well known Kelvin–Gibbs formula

$$kT \ln S = \frac{2M\sigma}{N\rho r}, \tag{26}$$

which also gives an expression[18] for ΔG. This was used for many years in the theory of nucleation, until a few years ago the criticism by Lothe and Pound[20-23] and also by their successors[24-26] cast doubt on the hitherto orderly set of ideas. The arguments of these authors changed from paper to paper under the influence of counter-arguments, but the general sense of the proposed revision of the classic theory was invariably that formula (25) describes the free energy of a drop having a fixed centre of mass, but not that of a nucleus endowed with external degrees of freedom and undergoing thermal motion in the space occupied by the condensing system.

In order to examine this question in detail, we must pass to the statistical-mechanical description of a multicomponent gas comprising a mixture of monomeric molecules and molecules aggregates of various sizes. The phase integral for such a mixture can be written

$$Q=\frac{1}{N!h^{3N}}\int \mathrm{d}^{3N}\boldsymbol{P}\int \mathrm{d}^{3N}\underline{r}\exp\left\{-\beta\left[\sum_i \frac{P_i^2}{2m}+U(r_1\ldots r_N)\right]\right\}, \qquad (27)$$

where P is the momentum of the molecule, U is the potential energy of interaction among all the molecules present, and $\beta = kT^{-1}$. We now express (27) in terms of the configurational partition functions for the individual nuclei, in which integration with respect to the coordinates is performed only over some bound region C, where each nucleus exists as a single bound group of particles:

$$q_g=\frac{(2\pi mkT)^{3g/2}}{g!h^{3g}}\int\limits_C \exp\left[-\beta U_g\right]\mathrm{d}^{3g}x, \qquad (28)$$

in which U_g is the energy of interaction of the molecules in a cluster.

The change to integration over bound regions itself causes discrepancies and, in the opinion of several authors, should be accompanied by the introduction of correction factors. However, the chief source of discrepancies is the mode of expressing q_g in terms of ΔG_g. If the chemical potential of a nucleus can be expressed

$$\mu = kT\left[\ln(q_g/N)-\ln(c_g/N)\right], \qquad (29)$$

it follows from the smallness of the difference between the Gibbs and the Helmholtz free energies that

$$c_g = q_g \exp(g\mu_1/kT). \qquad (30)$$

According to Lothe and Pound the quantity

$$\lambda_g = \exp(-G_g/kT);\ G_g = \Delta G + g\mu_1, \qquad (31)$$

is not identical with q_g but is a partition function for a spherical volume isolated in the massive liquid, occupied by g molecules, and provided with an interface. If in (30) we then use λ_g instead of q_g, we must introduce the correction factor

$$\Gamma=\frac{1}{N}\left\{\frac{q_g^{tr}q_g^{r}}{\lambda_g^{tr}\lambda_g^{r}}\right\}, \qquad (32)$$

termed[20-23] the "replacement factor", in which q^{tr} and q^{r} are the partition functions for the collective rotational and translational motion respectively of the nucleus, and λ^{tr} and λ^{r} are the corresponding partition functions for the spherical volume regarded as a drop with a fixed centre of mass. (The term "replacement factor" is sometimes applied to the product $\lambda_g^{tr}\lambda_g^{r}$.) Estimates of Γ based on reasonable values for the vibrational spectral parameters of the molecules in the liquid and for the moments of inertia of the nuclei give a correction of $\sim 10^{17}$ to the rate of nucleation.

Reiss and his coworkers[27-29], Lin[30], Stillinger[31], and also Rusanov and Kuni[32,33] correctly pointed out that the volume of liquid cannot be regarded as a drop with a fixed centre of mass, and that it is more correct to regard it as a drop having fixed boundaries. Because of the ability of the centre of mass of such a drop to fluctuate within its boundaries the replacement factor decreases to comparatively low values depending on the method used to estimate these fluctuations. On the basis of the earlier general theory of equilibrium in polydisperse systems[32] Rusanov and Kuni[33], as well as Parlange[34], showed that the difference between the free energies of formation of a freely moving drop and of a drop having fixed boundaries is almost equal to the difference between those of a mobile nucleus and of a drop having a fixed centre of mass. Certain analogies that can be drawn between the concepts of nucleation theory and those of nuclear physics indicate that the two models—a drop with fixed boundaries and a free nucleus--are in general identical, i.e. that $\Gamma = 1$. The model with fixed boundaries is indeed analogous to the shell model of the atomic nucleus, while the model of a free nucleus is analogous to the drop model. The identity of these models of the atomic nucleus has been demonstrated[35], at least at high temperatures.

In order to obtain agreement between calculated and experimental equations of state[36,37] the value of σ corresponding to the free energy of a planar surface per molecule must be replaced in (18) by values about 10% larger. Thus the surface tension must be correspondingly overstated in isolating the contribution of the collective motion of the cluster.

In the case of a fixed centre of mass ($\lambda_g^{tr} = 1$) the introduction of a replacement factor (allowing only for translational motion) is equivalent to multiplying q_g by $h^3/(2\pi gmkT)^{3/2}$. This view was most clearly expressed by Abraham[23], who, having isolated in the Hamiltonian of the nucleus the components corresponding to the collective translational and rotational motion, diminished by six the number of internal degrees of freedom over which the summation was made. From the equality of molecular momenta in gaseous and liquid phases at a given temperature Bashkirov and Sutugin have shown[38] that the restriction $\Sigma P_g = P$ is imposed on the range of integration in the evaluation of the phase integral over the components of the collective momentum from the momenta of the individual molecules constituting the cluster. The isolation in q_g^{tr} of a factor exceeding $g^{9/2}$ times the partition function for three internal degrees of freedom should then entail the division by $g^{9/2}$ of the partition function for the internal degrees of freedom. It is noteworthy that this approach was made by Frenkel' (though without comment) when, speaking of the need to allow for external degrees of freedom of the clusters, he replaced g by $g-2$ in both terms of Eqn. (25). The Lothe–Pound approach is equivalent to substituting $g-2$ only in the volume term. The equality of molecular momenta in liquid and gaseous phases in general supports the identity of the partition functions of the cluster and of a volume isolated from a liquid and provided with a surface: i.e. it indicates that formula (25) reproduces correctly the free energy of formation of a cluster whose physical properties coincide with those of a drop. However, several authors consider[31,39,40] that the configurational parts of the phase integrals for the cluster and for the volume isolated from the liquid differ somewhat, and there is also no unanimity on the magnitude of this difference. As already stated, however, the replacement factors obtained from the estimated configurational integrals are by no means so large as in the papers by Lothe and Pound.

A final comment on the replacement factor is that the Lothe–Pound approach leads to the conclusion that the concentration of free clusters in equilibrium with a given monomer concentration should far exceed the concentration of drops having a fixed centre of mass. Hence isothermal distillation of matter should take place from stationary to moving drops, which is obviously inconsistent with the law of the conservation of energy. The same argument can be used also in refutation of the identity of a cluster and a volume isolated from the liquid[38].

It is interesting[29,41] that in one case the replacement factor may indeed differ markedly from unity—in the formation of rigid spherical nuclei and molecules possessing non-degenerate rotation—when the factor should by less than unity. The possibility of the formation of solid, not supercooled liquid, nuclei from the vapour has not yet been proved; moreover, an aggregate of 20–90 molecules cannot be regarded as a smooth, rigid sphere.

The immense values of the Lothe–Pound replacement factor gave rise to many hypotheses on the nature of clusters to explain the discrepancy between the theory and experiment[42–47]. Since the Lothe–Pound theory is now obviously untenable, we shall not discuss these hypothesis further.

Two sources of uncertainty arise in connection with the coefficients β_g. Firstly, the density of clusters would be smaller than the macroscopic value ρ (see Section IV), so that the surface area of a cluster should be greater. Secondly, information is lacking on the coefficient of condensation $\gamma(g)$ on small clusters. It has been stated repeatedly that γ may diminish appreciably with decrease in size of the clusters. As long as we consider isothermal condensation (i.e. suppose that all the heat evolved in the system is immediately absorbed by the thermostat), however, it follows from the principle of detailed balancing that condensation and evaporation coefficients are equal. This implies that a decrease in γ should not affect the steady-state rate of nucleation, since from Eqns. (3), (5), and (6) we have

$$f_g = \frac{\beta_1\beta_2 \ldots \beta_{g-1}}{\alpha_2\alpha_3 \ldots \alpha_g} c_g, \tag{33}$$

and such coefficients occurring in β and α cancel out. Under completely isothermal conditions the decrease in γ with small clusters can affect only the time required to attain a steady state after the instantaneous establishment of supersaturation in a system comprising monomeric molecules. In practice the removal of heat of condensation is never instantaneous, which would influence significantly the course of elementary processes involving the smallest clusters, as the efficiency of collisions between vapour molecules and clusters drops sharply. Since the evaporation coefficient is an intrinsic property of the actual cluster, it is unaffected by non-isothermal conditions, and with small values of g the decrease in γ will lead to a decrease in I_0. These effects will be discussed in detail in Section VI.

Okuyama and Zung[48] tried to obtain an analytical expression for the dependence of γ on g. They started from the fact that γ should decrease with increase in the positive curvature of the surface, since the condensation of a molecule on a drop must involve work to increase the surface of the latter. However, one of the Reviewers has pointed out[49] that this is already taken into account by the Kelvin–Gibbs formula, and the Okuyama–Zung result is incorrect. The erroneousness of the latter formula is readily illustrated by applying it to condensation on a concave meniscus, when values of γ exceeding unity are obtained.

IV. PROPERTIES OF SMALL CLUSTERS

The evident doubt as to the applicability of phenomenological parameters, relating to major quantities of the condensed phase, to express the free energy of formation of clusters has stimulated a search for other methods of determining this function. The first attempts of this kind were based on the use in expressions for ΔG of surface tensions for a curved surface. A considerable number of such papers, reporting essentially modifications of Tolman's theory of surface tension, were surveyed in a previous review[50].

The one-sided character of these attempts was shown[51–54] by the demonstration that the decrease in tension of the curved surface of a cluster is accompanied by an increase in thickness of the interfacial layer with a consequent decrease in density of the droplets. Study of the asymptotic behaviour of the configurational integral of liquid droplets showed[55–57] that the free energy of a cluster cannot in general be written in the form $ag + bg^{2/3}$ and that expressions for ΔG should contain terms proportional to $g^{-1/3}$, $\ln g$, and—what is especially important—a term representing the contribution by capillary waves. It was also revealed[57] that the theory of the tension tensor in the interfacial layer, usually employed to determine the dependence of σ on surface curvature, is completely unable to reproduce the significant properties of clusters.

Decrease in the size of a cluster is not simply accompanied by a decrease in its density: the radial distribution of density in a cluster depends on its previous history and on the degree of saturation of the vapour—a conclusion reached by Strickfaden and de Sobrino[58], who calculated the density profile as a solution of the diffusion equation for molecules in the self-consistent field of the cluster.

Considerable efforts were concentrated on attempts to express ΔG in terms of the parameters of the intermolecular interaction potential for the molecules forming the cluster. Regarding a cluster as a polyatomic molecule, we can write

$$q_g = q_{tr}q_rq_vq_0, \tag{34}$$

where q_{tr}, q_r, and q_v are the translational, rotational, and vibrational partition functions respectively, while $q_0 = \exp(-U_0/kT)$, in which U_0 is the minimum potential energy of the cluster. If the cluster comprises polyatomic molecules, a factor must be included to allow for the contribtuion by intramolecular degrees of freedom. The main difficulties in solving such a problem are to determine moments of inertia, the set of frequencies, and the bonding energy. It is first necessary to assign a definite structure to the cluster; thus this approach is applicable only to crystalline nuclei. Yet several workers consider that direct formation of crystal nuclei from a vapour is impossible, since clusters are amorphous according to Ostwald's rule, and are able to crystallise only when they have become much larger than the critical size[59,60].

The first reported determination of q_g was made by Reed[61], who calculated it for nitrogen clusters on the assumption that the interaction of molecules in a cluster is described by a Lennard–Jones potential with clusters of each size existing in the most stable configuration (as dumbbells, regular triangles, tetrahedra, double tetrahedra, and cubes respectively). This method was modified by Andres[62] for clusters up to $g = 12$. Later papers specified only the lattice type, and interatomic distances were determined by finding the minimum potential energy.

Such calculations were made for argon clusters by Burton[63–65] and by McGinty[66], who both calculated the rate of nucleation by means of formula (14) and obtained agreement with calculations based on the classical theory and the surface tension of solid argon. In contrast to the classical theory, quantum-mechanical calculations predict several characteristic properties for clusters, e.g. an anomalous size dependence of heat capacity, and a non-monotonic dependence of q on g. Abraham and Dave[67–69] showed that results identical with those of Burton and of McGinty can be obtained more simply by calculating the thermodynamic properties of crystalline clusters by means of the Einstein theory of the heat capacity of crystals extended to a system bounded by an interface.

Burton's most recent calculations[70] of rates of nucleation in argon vapour, based on quantum-mechanical calculations of ΔG, differ markedly from the predictions of the classic theory: over the range of supersaturations 12–72 and at reduced temperatures of $T/T_{cr} = 0.35–0.47$ the ratio of his values of I to the classical values increases from 10^{-2} to 10^7. Bonissent and Mataftschiev[71] made similar calculations for an arbitrary model substance whose molecules interacted in conformity with a Lennard-Jones potential. Having calculated the equilibrium concentrations of hexagonal clusters of 2–14 atoms, they also computed the surface tension for crystals of the same model molecules, and from this latter value found the classic equilibrium concentrations. Good agreement was found between such pseudoclassical calculations and rates of nucleation calculated in terms of the intermolecular interaction potential. These authors concluded that the possible existence of different configurations of the clusters does not affect significantly the values of c_g, but Burton[70] holds the opposite view.

It is interesting that the process of selecting configurations for clusters by successive approximation to the configuration corresponding to minimum free energy involves significant distortion of the lattice assigned *a priori* to the clusters. Use of the Lennard-Jones potential yields especially considerable distortions of crystal structure for $g = 13$ and 55.[72] Use of the Morse potential in the calculations encountered the same difficulty[73–75]. It was concluded that this problem is complicated by taking long-range forces into account, and this is what prevents the application of quantum-mechanical calculations to clusters containing $>$100 atoms.

The impossibility of achieving crystalline structures in clusters is probably the reason for the frequent observation of amorphous disperse condensates. This supports the concept[76] that subcrystallites consisting of a few atoms appear before particle formation. A cluster formed from such subcrystallites cannot have a crystalline structure.

Quantum-mechanical calculations for molecular aggregates in the vapours of several metals[77] do not give good agreement with experimental results even for a dimer: adjustment with the aim of improving agreement for the bonding energy increases the divergence of vibration frequencies, and conversely. Nevertheless, these results were used for calculations of bonding energy in Ag_g and Pd_g complexes, for which great stability of linear and cyclic aggregates was predicted in comparison with aggregates having a three-dimensional structure[78].

Relatively numerous attempts have been made to calculate aqueous clusters. Inspection of results obtained by various workers[79] indicates that the properties of the dimer can be calculated quite well. Large clusters, however, exhibit discrepancies both in quantitative estimates of bonding energy and in the determination of the relative stability of linear and cyclic structures. Del Bene and Pople[80] found that cyclic clusters are the more stable, supporting this conclusion by the presence at 3.5 Å in liquid water of a maximum in the radial density distribution function, a position which can be interpreted as the distance along the diagonal in the cyclic tetramer[81]. Recalculation of cyclic clusters[82] suggested absence of the non-additivity of bonding energy which might have been responsible for their great stability, so that linear aggregates should be the more stable, the correctness of the calculation being illustrated by prediction of the true bonding energy of ice. The linear structure of water complexes is suggested by experimental observations[83] on the magnetic focusing of beams of molecular aggregates.

Plumer and Hale[84] calculated clusters containing up to 57 H_2O molecules, and arbitrarily chose a cyclic pentamer as unit cell. They assumed that a cluster has an ordered structure, as indicated by the existence of hydrogen-bonded complexes in liquid water. Nevertheless, the Hagler–Scheraga–Nemethy theory of the structure of liquid water[85] in fact interprets water as a mixture of clusters of different sizes, but the maximum in the size distribution function occurs at $g = 4–5$, and clusters larger than 50 molecules are completely absent from the liquid phase. A nucleus in the vapour phase, consisting of tens of molecules, is therefore also more logically regarded as a complex of smaller clusters of hydrogen-bonded molecules bound together by van der Waals interactions. The values obtained[84] for ΔG are scattered on both sides of the classic ΔG–g curve. This scatter would obviously have been diminished by taking into account the existence of a large number of ruptured hydrogen bonds in the cluster.

The possible existence of different geometrical configurations for clusters of a given size makes it necessary to consider the statistical contribution made to q_g by each configuration. The growth of clusters under such conditions should be regarded, strictly speaking, not as unidimensional diffusion along an axis but as displacement in a multidimensional space. Ziabiki[86] deduced a multidimensional kinetic equation of nucleation, the dimensions of which were equal to the number of faces on the cluster–nucleus. Semenchenko and Petrovskii[87] were able to reduce this equation to a one-dimensional form by using Semenchenko's thermodynamic theory of small crystals[88], enabling ΔG to be expressed in terms of the Wulf constant. In the view of these workers anisotropy of the crystal nucleus should have little effect on the magnitude of ΔG.

Equilibrium concentrations of dimers have been calculated not only in Refs. 61 and 62 but also in Ref. 89, in which the Morse potential was used for argon and krypton. The dynamic equilibrium in a system containing monomeric and dimeric molecules has been examined[90]: the concentrations of three types of bound states—stably bound, metastably bound, and dissociating—were calculated for various gases over a wide temperature range by use of the rectangular-well and Sutherland potentials. The temperature dependence of c_2 obtained at low temperatures was closely similar to the results of calculations by Reed's method[61], but the discrepancy increased with rise in temperature. Divergence between results in Refs. 89 and 90 was slight. In a monomer–dimer system not in contact with a thermostat the temperature of the dimer is below, while that of the monomer is above, the average temperature of the mixture[91]. Even when this effect is taken into account, however, the concentration of dimers is similar to that calculated by Stogrin and Hirschfelder[90].

V. NUCLEATION UNDER NON-STATIONARY CONDITIONS

Two cases of non-stationary nucleation can be distinguished: either supersaturation is established instantaneously and then remains constant, or it varies continuously throughout the process. A steady state may be established in the former case, but some time is required for the concentrations to become steady, and during this period the rate of nucleation will increase from zero to the steady value I_0. Several workers investigated the time of attainment of a steady state[92-96] by solving the time-dependent equation for the diffusion of nuclei along the size axis with the initial conditions $c_1 = 1$ and $c_g = 0$ with $g \neq 1$. The rate of nucleation under non-stationary conditions was shown to be related to the steady value:

$$I(t) = I_0 \exp(-\tau/t), \tag{35}$$

where

$$\tau = A(\beta_1 c_1 S_g)^2 Z,$$

is the relaxation time of nucleation, in which A is a numerical coefficient estimated by various authors to lie within the range $\frac{1}{4}(1-\pi)$.

Abraham[97] used a computer to solve Eqns. (2) with the aim of studying non-stationary nucleation at a constant supersaturation S, and his results indicated the analytical solution in Refs. 95 and 93 to be the most accurate. Similar values of τ were obtained[98] in a numerical tabulation of the solution of the equation of non-stationary diffusion in quadratures. Computer calculations by Courtney[92] indicated rather slower establishment of a steady state, probably because of his use of a different expression for c_g.

Abraham also investigated the effect of the cluster-size dependence of the condensation coefficient on the time of establishment of the steady state. Although the erroneous Okuyama–Zung formula[48] for the γ–g dependence was used in these calculations, the results give an idea of the possible influence of this factor. According to Abraham's calculations[99] the concentration of clusters considerably smaller than the critical size approaches steady values, passing through a maximum; the concentrations of clusters of near critical sizes increase monotonically to steady values.

If the change of supersaturation during the process is sufficiently slow, the cluster concentrations may have time to assume the steady-state values for the instantaneous temperature and monomer concentration. Raizer[100] deduced a criterion of slowness in the variation of supersaturation for the adiabatic expansion of a cloud condensing in a vacuum.

It can readily be seen that a steady state is attainable only in cases of slow nucleation. Rapid and intermediate types of nucleation are usually accompanied by rapid change in the external conditions. In this case the description of condensation should be based on numerical integration of the set of equations for the concentration variation of critical and subcritical clusters together with the equations for the concentrations of monomer and supercritical species[43]. Methods have been published[16,19] for reducing the number of equations of type (2) to a reasonable level permitting numerical integration on modern computers.

VI. NUCLEATION UNDER NON-ISOTHERMAL CONDITIONS

The theory outlined in Section II describes an isothermal process: i.e. it is based on the hypothesis that the mixture of clusters and monomeric molecules is in contact with a thermostat that will instantly level out local variations in temperature. In real systems the role of such a thermostat can be played only by an uncondensable carrier gas, which dilutes the vapour of the condensable component. Energy is transferred by collisions between carrier-gas molecules and clusters, i.e. at a finite rate. Several non-isothermal effects during condensation arise from the finite rate of energy exchange and the finite number of molecules of the carrier gas[101]: firstly, the mean temperature of clusters of a given size is higher than that of the mixture, with a consequent increased probability of evaporation; secondly, the non-instantaneous removal of the excess of kinetic energy of the condensing molecules may diminish the efficiency of primary acts of addition of molecules to small clusters.

Application of the theory of rate processes to condensation[102] indicates that the transfer of molecules from the vapour to the condensed phase is preceded by formation of an activated complex on the surface. This complex may either dissociate with re-evaporation of the molecule or undergo deactivation, when the molecule will pass into the condensed phase. In the case of a flat surface and sufficiently large clusters deactivation of the complex takes place by the exchange of energy with the condensed phase, the consequent rise in whose temperature is too small to cause immediate vaporisation of another molecule. Deactivation of very tiny clusters can result only from collision with carrier-gas molecules or with molecules of the vapour at the cold end of the energy distribution. In the limiting case of formation of a dimer from two single molecules, a third body must be involved in the collision. Since three-body collisions take place far less often than two-body collisions, the rate of growth of small clusters should be considerably lower than is assumed in the isothermal theory. Furthermore, if nucleation occurs while the temperature of the vapour is falling or immediately after rapid cooling, the temperature relaxation of the clusters will be slower than for free molecules.

Salpeter has recently[103] distinguished three cases of non-isothermal growth of clusters determined by the conditions

(i) $c_p k \gg B/kT$ (large clusters)
(ii) $(B/kT)^2 \gg c_p/k \gg B/kT$ (intermediate clusters)
(iii) $c_p/k \ll B/kT$ (small clusters)

where B is the heat of condensation per molecule, and c_p is the heat capacity of a cluster. By supposing that the temperature of a cluster relaxes exponentially after addition or vaporisation of a molecule, he obtained an expression for the non-isothermal rate of growth of a cluster as a function of a parameter representing the thermal relaxation of clusters and supersaturation. For large clusters a formula for rate of growth was obtained that had been deduced earlier[104]; it predicted that the rate of addition of molecules to clusters during the condensation of water in a Wilson cloud chamber should be much smaller than in the isothermal approximation. The rate of growth found for intermediate clusters from the average temperature of the clusters is zero: i.e. their growth is possible only because of the presence of a temperature distribution both of clusters and of molecules. Salpeter considered that small clusters could grow during rapid cooling only by the addition not of single molecules but of dimers, from which one of the molecules subsequently vaporised.

As already mentioned in the account of the isothermal theory, its construction on the basis of equilibrium thermodynamics is an approximation, the crudeness of which increases with penetration into the region of metastable states. The use of the Szillard–Farkas model to describe non-isothermal nucleation was until recently not justified at all. However, Bashkirov and Novikov[105], using the non-equilibrium statistical operator method[106], have demonstrated that the notation based on the diffusion of clusters along the size axis can be used also to describe non-isothermal nucleation. In the Reviewers' opinion, nevertheless, this conclusion can relate only to "large" clusters in Salpeter's classification.

The presence of a large excess of a carrier gas relative to the vapour concentration is frequently accepted as the sole criterion of the isothermal character of nucleation. However, the relative departure from isothermal conditions at a constant concentration ratio of carrier gas to vapour n_0/c_1 may vary with I, because the rate of evolution of heat of condensation on nuclei of a given size is proportional not to $\beta_{1g}c_1$ but to the flux $I = f_g(\beta_{1g}c_1 - \alpha_g)$. Thus the isothermal criterion should be

$$\varepsilon = \frac{\beta_{ng}n_0}{\beta_{1g}c_1 - \alpha_g}, \tag{36}$$

where β_{ng} is the coefficient of collisions between molecules of the inert gas and clusters.

Unfortunately, it is not yet possible to predict by calculation the values of ϵ for which the isothermal approximation could be used, but certain rough estimates may serve as guide. Firstly, the thermal relaxation of polyatomic molecules requires 10^3–10^4 collisions with molecules having the equilibrium energy distribution. On the other hand, Katz[107] made an experimental study of the effect of the quantity of carrier gas on the rate of nucleation in a diffusion cell, and found that I was unaffected if the gas pressure was 50% greater than that of the condensing vapour. Adopting $c_1 \simeq 5 \times 10^{17}$ cm^{-3}, $\beta_{ng} \simeq 10^{-10}$ cm^3 s^{-1}, $I = 1$ cm^{-3} s^{-1}, and Abraham's calculation[97] of $f_g = 10^7$ cm^{-3}, we obtain $\epsilon \simeq 5$. From this last estimate it may be concluded that, with the carrier gas at atmospheric pressure, nucleation is isothermal in character only when $I < 10^2$. It should be noted that Katz was dealing with vapours comprising polyatomic molecules the heat capacity of each of which already exceeded the heat of condensation. In the condensation of monatomic or diatomic molecules the condition $\epsilon \simeq 1$ would be insufficient to ensure isothermal conditions.

Thus the isothermal approximation for nucleation has a very restricted range of application, although it is very often used for comparison with experiment and for engineering calculations under definitely non-isothermal conditions. However, a theory of non-isothermal nucleation has not yet been worked out. Construction of such a theory requires in general consideration of the diffusion of clusters in the size–energy phase plane (which is also approximate, since the possibility of different redistributions of energy between degrees of freedom of the cluster is ignored). Examination of the continuous spectrum of energy states of clusters has not yet been applied, but attempts have been made to replace averaging of the energy state by the division of clusters into two groups, at the equilibrium temperature and activated respectively. Hagena[108] tried to solve a set of differential equations in which the concentrations of activated and relaxed clusters were considered separately, and their interconversion was taken into account. Other workers[109] also discussed two types of states of clusters, but incorrectly neglected the possible evaporation of molecules from thermally relaxed clusters.

On the whole the theory of non-isothermal nucleation still remains in an unsatisfactory state.

VII. EXPERIMENTAL METHODS FOR THE STUDY OF SPONTANEOUS CONDENSATION AND INTERPRETATION OF THE RESULTS

The chief parameters used in the theory of nucleation—rate of nucleation, equilibrium concentrations of nuclei, size of critical nucleus, and free energy of their formation—cannot be measured experimentally. Experiments provide information only on the new phase: its formation when a certain supersaturation is reached is confirmed, the particle size and concentration of the condensed phase are indicated, and in the most favourable case data on the variation in particle size and concentration during condensation are obtained. Such information can be used for comparison, not with the actual theory of nucleation, but only with certain models calculated by use of the theory. Since such models themselves involve various postulates and errors, additional uncertainty is introduced into the problem of agreement between theory and experiment.

The Wilson chamber has been used longest for the study of spontaneous condensation. For decades it has been employed simply to confirm the formation of a disperse phase on attainment of a certain supersaturation, regarded as critical and compared with that predicted by theory. Measurement of the concentration of droplets formed was usually omitted, and the time during which supersaturation was maintained at the critical level was merely estimated. During recent years cloud chambers have been produced enabling a constant temperature to be maintained by means of a programmed expansion cycle lasting tens of times longer than in simple cloud chambers[110,111]. It was found that expansion was adiabatic only in sufficiently large chambers[112]. In view of statements on the possible evolution of foreign condensation nuclei from the walls of the chamber following reaction with atmospheric oxygen[59], experiments began to be made in pure inert gases, and materials for the manufacture of the chambers were chosen more carefully. Reasons were established why the critical supersaturation was lower for repeat expansions: droplets formed in the first cycle had insufficient time to evaporate during the compression period[113].

The most recent work with a Wilson chamber has followed the time variation of the degrees of dispersion and the particle concentration, either by measuring the intensity of scattering of a monochromatic beam of light or by high-speed microcinematography with dark-field illumination. In the former case the mean size is obtained by comparing the measured absolute intensity scattered at a given angle with calculations based on the Mie theory; measurement of the angular dependence of the polarisation ratio of light scattered by the particles will give the width of their size distribution[114-116].

Comparison of theory with experiment at only the one, critical supersaturation, although giving less information, is logically more soundly based, since it describes more correctly the metastable state of the vapour, not the breakdown of this state. However, the need to establish methods of calculation for engineering bulk condensation compels the use of nucleation theory even to describe processes in which nucleation takes place on a background of exhaustion of the vapour. Allowance for the decrease in supersaturation due to consumption of the vapour was first proposed by Tunitskii[117]. A more accurate method, requiring simultaneous numerical integration of the equations of adiabatic expansion, nucleation, and condensation growth of particles, was suggested by Courtney[118] and then used in many papers for the interpretation of experimental results,

A method for the study of bulk condensation—the diffusion cell—has recently been used very successfully by Katz[120,121] following its early first application[119]. Gradients of temperature and vapour concentration are established between two plates (by evaporating the vapour from the hot plate and condensing it on the cold plate). Because of the non-linear temperature dependence of the vapour pressure the vapour becomes supersaturated at some distance from the hot plate, and the supersaturation may exceed the critical value. Formation of the condensed phase can then be detected by the usual methods. In contrast to the Wilson chamber, condensation here is a steady-state process, which is a great advantage. Furthermore, the diffusion cell is self-purifying: i.e. various impurity centres of condensation are immediately removed by the condensing vapour. In this case comparison of theory with experiment reduces to calculating the height distribution of supersaturation, determining the level at which mist is formed, and thus finding the critical supersaturation.

Just as in the Wilson chamber, supersaturation by adiabatic cooling is produced during supersonic flows of vapour and vapour–gas mixtures through a nozzle. Investigations of condensation under such conditions have become widespread because of the great interest for energetics presented by the possibility of controlling formation of the disperse phase. Condensation is studied by measuring the static pressure distribution along the axis of the nozzle (formation of a condensed phase is accompanied by a change in pressure), by observing the flow with shadow optical instruments (schlieren) and by measuring the scattering of a laser beam in different cross-sections of the nozzle. The last method will now detect the formation of particles of mean size 20 Å.[115] Many studies have now established agreement between the mass of the condensed phase calculated from changes in the static pressure and from light scattering[114,122]. Results of the determination of the mass of the condensed phase or of the mean size of the particles and their concentration are compared with those of the simultaneous numerical solution of the equations of the conservation of mass, energy, and momentum, the equation of state, and the equations for the number of particles

$$\mathrm{d}n_g/\mathrm{d}t = I(t) \tag{37}$$

and for particle growth by condensation. Such a set of equations was first used and solved analytically with several simplifications by Oswatitsch[123]. More accurate methods requiring numerical integration have been described by several authors[124-126]. Especially noteworthy is the work of Campbell and Baktar[124], whose methods of calculation yield not only the mean particle radius but also the size distribution, since separate kinetic equations are written for the growth of particles formed in different portions of the flow. In the Reviewer's opinion, however, these authors made several unnecessary postulates (e.g. neglect of the growth of nuclei beyond the critical size in the zone where they had been formed). In calculations on condensation most authors use free molecular rotations in the kinetics of the growth of particles and the transfer of heat to them, which is incorrect, since with particle growth the Knudsen numbers characterising the régime of heat and mass transfer to the particle become too small for free molecular rotations to remain applicable. However, the main complexity in the use of nucleation theory for such calculations is the great non-uniformity and non-isothermality of the process when the vapour escapes in the absence of a carrier gas.

Adiabatic cooling of a gas takes place also in so called high-intensity molecular beams, which are fine, supersonic jets emerging into a high vacuum, from which the central portion of the flow is isolated by means of a set of conical diaphragms[127]. Very rapid and strong cooling is achieved in such flows. Formation of molecular aggregates comprising tens, and sometimes even thousands, of molecules can be detected by means of ionisation detectors, as well as by time-of-flight and quadrupole mass spectrometers. Information on the size of clusters formed in molecular beams can be obtained from measurements on its weakening by a cross beam. Measurement of the weakening of the latter beam will also give the fraction of monomer uncondensed. Such a method was used to study the agglomeration of clusters after complete exhaustion of the monomer[128], i.e. essentially coagulation in the beam.

The state of the internal degrees of freedom of molecules in such beams is very far from equilibrium: their vibrational, rotational, and translation temperatures may differ several-fold. Thus the formation of clusters of polyatomic molecules in such beams has little in common with the concepts of nucleation theory. The main use of such experiments is to provide information on the primary acts in the aggregation of monatomic molecules and on the possibility of the formation of mixed molecules aggregates by the condensation of multicomponent systems. The interpretation of data obtained by means of powerful molecular beams is complicated by the inability of existing escape theories to explain certain qualitative features—e.g. the presence of maximum intensity at a certain distance along the beam between the nozzle and the first conical shield (skimmer)[129,130] and the angular separation of components differing in mass.

Cooling during the molecular diffusion of a vapour through a cold gas takes place in certain forms of equipment for the production of metal powders. Such experiments give some useful information on the condensation of metal vapours. Similar results are obtained in experiments on exploding wires, in which cooling is due both to the diffusion mixing of the vapour with the surrounding gas[76,131].

Several studies have been made on condensation during the turbulent mixing of a hot vapour–gas mixture and a cold gas. The Reviewers have shown[132] that calculation of condensation in turbulent flows must take into account the three-dimensional transport of clusters by the turbulent vortices, so that Eqns. (2) for the description of nucleation must be replaced by the set of partial differential equations

$$v\,\mathrm{grad}\,f_g = \mathrm{div}\,(D_t \mathrm{grad}\,f_g) + I_g, \tag{38}$$

where v is the time-average rate of flow, I_g the operator of the right-hand side of Eqn. (2), and D_t the coefficient of turbulent diffusion.

Another peculiarity of the condensation consists in the effect of turbulent pulsations of temperature and concentration. Pulsations lasting longer than the relaxation time of deviation may obviously distort significantly the course of condensation, but this aspect has not yet been investigated. In spite of these complicating factors, it is necessary to investigate condensation in turbulent flows, because such processes are often met in technology. Furthermore, turbulent mixing is convenient for the study of condensation at high temperatures. The above complications disappear when mixing precedes condensation, i.e. with rapid mixing and slow condensation—and hence at low vapour concentrations—even if condensation may be of the "rapid" type.

A one-dimensional approximation was suggested[13,14,16] for calculating condensation in a submerged turbulent jet. This involves numerical integration of an equation, averaged over time and angle, for rate of mixing and a set of equations (2) for the concentrations of small clusters, as well as equations for the growth of superciritcal particles of average mass. In another modification of this method, applicable to processes in which coagulation predominates, Eqns. (2) are combined with the coagulation equations of the Rosinski–Snow model[133]. Amelin et al.[134] suggested a method for studying condensation during turbulent mixing, in which nucleation and enlargement of the particles took place in different apparatus, so that there was no need to consider exhaustion of the vapour during nucleation. Equipment in which a vapour-gas mixture is diluted by a coaxial flow of a cold gas in a diffuser with cooled walls has been used[135] to study condensation in a turbulent flow; these experiments were interpreted on the assumption that condensation is preceded by mixing.

Shock tubes have also been used for the study of nucleation. They may serve two purposes: in some cases[136] vapour condensers in the rarefaction formed behind the detonation front; in other cases the heating effect of the detonation wave causes decomposition of a chemical compound with formation of a non-volatile component, whose condensation is studied[137].

VIII. EXPERIMENTAL RESULTS ON SPONTANEOUS CONDENSATION

The large majority of experimental results, including those on the condensation of one-component systems, compare with the predictions of the isothermal theory, although isothermal conditions are not always observed even when condensation is studied in the presence of a carrier gas. In Wilson chambers possible non-isothermal effects become more intense with rise in the initial temperature.

Calculations based on the classic theory[118,141] agree with results on the condensation of water[110-112,138-140] only within a narrow range of supersaturations. On the whole the experimental dependence of rate of nucleation on supersaturation has a smaller slope than the theoretical curve, and intersects the latter at $S = 5$. Observations on the establishment of a steady state in Wilson chambers indicate a slower increase in I than is predicted by Courtney's calculations[118] or else agree with them only at low temperatures[138]. We recall that these calculations[118] use a formula for I which is smaller by the factor $1/S$ than that obtained by Frenkel'. The slower experimental attainment of a steady state may indicate either that the condensation coefficient is lower with small nuclei or that the process is non-isothermal.

Special attention should be given to the extremely thorough and carefully conducted work by Kassner and his coworkers[110,111,140], in which the rate of nucleation was measured as a function of supersaturation for several temperatures by the use of various inert carrier gases. These results are fully consistent with those obtained earlier, and support all the earlier conclusions, but cover far wider ranges of temperature and supersaturation. Among the important conclusions reached by these workers was that, when the supersaturation is maintained constant after expansion, the rate of formation of new particles does not remain constant, but diminishes, the effect becoming more marked with increase in supersaturation. This phenomenon was explained by the presence in water vapour of molecular nuclei, whose concentration is proportional to that of the vapour. The I–S curve has a point of inflexion in the range $I = 10$–100 cm^3, which is most clearly defined at low temperatures. The experimental curve generally intersects the curve calculated on the classic theory, so that the rate of nucleation is underestimated at low supersaturations, and overestimated at high supersaturations. On the other hand too high rates at low supersaturations are explained by the substantial contribution of heterogeneous condensation on molecular condensation nuclei. Rates are distinctly greater in heavy than in light inert carrier gases.

Allard and Kassner[110] attributed the formation of foreign nuclei to the radiolysis of water vapour by the background cosmic radiation. The heterogeneous character of condensation at low supersaturations most probably applies to all other experiments on the condensation of water in Wilson chambers. The difference between results obtained in argon and in helium was explained on the hypothesis that these gases form clathrate compounds with water, of which the argon clathrates are the more stable. The untenability of this hypothesis was shown by Burke[142], who also suggested possible mechanisms of the radiation formation of foreign nuclei and pointed out that argon, which should act as a third body in several of the reactions involved, will ensure a greater cross-section of three-body reactions than will helium, which explains the difference in the kinetics of condensation in these gases. Moreover, argon promotes more rapid removal of heat from nuclei than occurs with helium, as follows from Luke's calculations[143]. Clark and Noxon[144] reported the formation, under the influence of ionising radiation in helium containing unsaturated water vapour, of particles reaching 10^{-4} cm. This also supports the heterogeneous character of condensation at low supersaturations. The formation of aggregates $Ar_x(H_2O)_y$ was reported[145], but at far lower temperatures than in the experiments of Allard and Kassner.

The point of inflexion on the I–S curve was explained by White and Kassner[146] on the hypothesis that an electrical double layer is formed on the surface of aqueous clusters by the orientation of water-molecule dipoles. Such a point was indeed present on the dependence of rate of nucleation on supersaturation which they obtained by using a formula for ΔG allowing for the contribution by a double layer, but this contribution was only estimated.

The temperature dependence of the critical supersaturation was studied on methanol, ethanol, water, hexane, octane, nonane, and heptane by Katz and Ostermeyer[120] and by Katz[121]. The hot plate, from which vaporisation occurred, was located at the bottom of the diffusion cell used, so that, to avoid mixing by convection currents, the temperature gradient had to be balanced by a composition gradient in the vapour–gas mixture, with a light gas (hydrogen, helium, or neon) at reduced pressure employed as carrier. As a consequence, the concentration ratio of vapour and carrier gas was still lower than is usual in Wilson chambers, which is dangerous to isothermal conditions. However, this aspect might be unimportant, since most experiments were made with polyatomic substances, for which the difference in heat capacity between condensed and vapour phases is relatively small. For organic compounds these workers obtained very good agreement with the classic theory in the Becker–Döring form; for water, however, as in Wilson chambers, agreement was observed only over a narrow temperature range and with considerable scatter.

Reiss and Heist made accurate measurements of the critical supersaturation of water vapour in a diffusion cell over a wide temperature range[147]. Their results show little experimental scatter and give S_{cr} values 8% above those predicted by the Frenkel' formula. In contrast to measurements in a Wilson chamber, the nature of the carrier gas is of no significance in a diffusion cell. This indicates truly isothermal conditions and the absence of foreign nuclei, whose formation involves molecules of the inert gas.

Formation of a condensed phase during supersonic flows of a one-component vapour, of course, cannot be described on the basis of the isothermal theory. It is not surprising, therefore, that the large majority of results for the condensation of water vapour in nozzles can be reconciled with calculations based on the classic theory only after the introduction of empirical parameters. A single parameter, e.g. a condensation coefficient less than unity, is insufficient to obtain the correct form of static pressure curve. Therefore two or three parameters are generally employed[124,148–151].

Non-isothermal conditions are not in general the sole factor casting doubt on the use of steady-state solutions of the classic theory to describe condensation in nozzles. The large supersaturations and the small critical nuclei indicate that the processes occurring in nozzles belong to the rapid type of nucleation. Introduction of a correction for the non-stationary character of the process in these cases is equivalent to adjusting the condensation coefficient, and by itself, therefore, cannot improve the agreement with calculations.

In contrast to the above results the later papers by Wegener and his coworkers[114,152] on the condensation of water vapour gave good agreement with the classic theory for liquid nuclei with $\gamma = 0.01$. In his earlier papers Wegener[153,154] had obtained agreement only by adopting lower values for γ and postulating that the nuclei had a crystalline structure.

A group of investigators[155,156] studied the condensation of the vapours of water, benzene, chloroform, and trichlorofluoromethane at partial pressures of 0.01–0.1 mm in air emerging through a Laval nozzle. At low supersaturations the rate of condensation of water was predicted satisfactorily on the basis of the classic theory with $\gamma = 0.01$, but the organic liquids condensed significantly more rapidly than might have been expected from calculations with $\gamma = 1$. These results may be affected by the presence of impurities, most likely water. The same workers found[156] that 0.001% of water greatly accelerates the condensation of ammonia, which is explained by the greater rapidity of binary nucleation.

Great interest attaches to the non-stationary jumps in condensation occurring in Laval nozzles, a phenomenon studied in detail by Deich et al.[157] and given a theoretical explanation[158,159]. The jump in density preceding the jump in condensation moves upstream into the subsonic zone, as a consequence of which the jump in condensation moves downstream, until the effect of the former jump on the flow parameters becomes negligible and jumps reappear at the previous sites. The frequency of the oscillations in the position of the condensation jump reaches 1 kHz. This phenomenon illustrates clearly the non-isothermal character of condensation in nozzles. A peculiar type of condensation with adiabatic cooling was predicted by Deich and Filippov[159] and investigated experimentally by Deich et al.[160]; it involved condensation by turbulent perturbation of a subsonic unary flow, in which the supersaturation was considerably less than the critical value.

A considerable number of studies with Laval nozzles were made on condensation in the presence of two condensable components. However, the thermodynamic properties of the components frequently differed so greatly that the start of condensation of the more volatile component was preceded by formation of large drops of the less volatile component. Hence the results relate to heterogeneous condensation rather than to homogeneous binary nucleation. The condensation of mercury is accelerated by the introduction of rubidium vapour and of nitrogen, as well as on the addition of argon[161]. The need to use higher values of σ to bring calculation into agreement with experiment gave rise to hypotheses[42–66] as to the structure of aqueous clusters, which should actually have possessed a surface tension greater than σ_0. In the Reviewers' opinion the divergence of theory from experiment has other explanations—non-isothermal and non-equilibrium conditions, decrease in γ with small nuclei, non-monotonic dependence of the free energy of formation of nuclei on their size.

Experiments[134] on the condensation of water vapour with turbulent mixing of flows at the same temperature gave a result analogous to those obtained by other methods: the rate of nucleation exceeds the theoretical value at low supersaturations, but is smaller at high separations. The same situation has been observed for the vapour of dibutyl phthalate.

Study of the rapid type of nucleation is still more complicated than that of the slow type, since in this case a relatively short period of nucleation is followed by coagulation, which begins when even the coarsest particles of the condensed phase do not exceed 100 molecules[13]. Because coagulating systems tend to "forget" their initial state, it is difficult to reach any quantitative conclusions on the process of nucleation. In such a case the only requirement of theory is a reasonable estimate of the lag in the early stages of the agglomeration of vapour molecules relative to systems in which avalanche condensation takes place with 100% collision efficiency.

Some idea of the character of rapid nucleation could be obtained from studies on the condensation of very dilute inorganic vapours and the mechanism of the formation of highly disperse uncoagulated aerosols[162–164]. It is well known that such aerosols of low number concentrations can be obtained when a gas flow passes over the heated surfaces of metals, their oxides, and their salts. Calculation shows that the critical nucleus is very small in such cases, most probably a dimer, whose condensation provides a typical example of the second type of nucleation. The aerosol obtained would be of coagulation origin: i.e. with short lifetimes of the condensing system the number concentration is high and the scatter of sizes large. The experimental observation of relatively monodisperse aerosols of low number concentration can be explained only by the heterogeneous origin of the particles. The problem remains as to why homogeneously formed particles are not observed in these experiments. The only possible explanation is the dependence of the efficiency of collisions of vapour molecules with clusters on the size of the latter, which has been discussed in Section IV. Computer experiments simulating agglomeration of a vapour involving such a dependence showed that the induction period in the formation of homogeneous particles may be sufficiently long for the vapour to condense on the walls before the appearance of particles formed by homogeneous condensation. Since the length of the induction period decreases with increase in the initial vapour concentration, it may be expected in some cases that particles may, nevertheless, be formed by condensation, but they will be significantly smaller than those resulting from heterogeneous condensation on impurity nuclei.

This prediction has been confirmed experimentally[16,163] for the vapours of silver, sodium chloride, and silver iodide. It is interesting that the difference in size between particles formed homogeneously and heterogeneously was quite large in the agglomeration both of monatomic and of diatomic molecules: i.e. formation of a dimer of a diatomic molecule also requires the participation of a third body. The possible dissipation of excess kinetic energy in an internal degree of freedom of the diatomic molecule is evidently insignificant.

The fact that formation and growth of the smallest clusters are possible only as a consequence of three-body collisions will explain the dependence of particle dispersion on experimental conditions. The decrease in particle size as the gas pressure falls in the diffusion of metal vapours through rarefied inert gases[16,131,165] can be attributed to the increasing rarity of three-body collisions and the attainment of the earlier stages of agglomeration. The increase in dispersity when argon is replaced by helium is explained similarly: the latter is less efficient as a third body, which also slows down agglomeration. The fact that from a certain point further decrease in gas pressure has no effect can be attributed to the coalescence of fine particles after their deposition on the walls.

Considerable understanding of the course of the early stages in the aggregation of molecules has been provided by experiments on high-intensity molecular beams. Miln et al.[166] compared the results of computer experiments simulating the kinetics of dimerisation in a fine supersonic jet of argon with the measured concentrations of dimers, and found that at sufficiently low temperatures the termolecular rate constant is similar in order of magnitude to that calculated for the three-body collision cross-section of solid spheres. However, the strong temperature dependence of the constant suggests that not all three-body collisions result in formation of the dimer. The dissociation constant of the dimers was estimated in this work by the method of Stogrin and Hirschfelder[90]. Golomb et al.[167] found $k_3 = 3\times10^{-33}T^{1/2}$ for the termolecular dimerisation constant of argon; the concentrations of dimers were 25–50% of the equilibrium values calculated according to Stogrin and Hirschfelder.

Concentrations of dimeric argon closely similar to those calculated by this method were observed by Milne[168]. The addition of nitrogen and argon to a jet of carbon dioxide has the opposite effect on the kinetics of the formation of clusters. His explanation was that the drop in temperature of the escape of nitrogen into a vacuum is slower than with argon, so that dimers of the latter are more effective as third bodies in the collisions of carbon dioxide molecules. The rate of formation of dimers in an argon beam was greatly diminished by additions of polyatomic molecules. Mixed clusters Ar_xH_2O and $Ar(H_2O)_x$ were detected. Henkes[169] established by mass-spectrometric analysis of products from the condensation of carbon vapour that the concentrations of clusters decrease non-monotonically with increase in their size. This can probably be attributed to a non-monotonic variation in the free energy of formation of clusters with their size.

Hagena and Obert[170] found that similarity was observed in the condensation of neon, argon, xenon, krypton, nitrogen, and carbon dioxide in a supersonic jet. In particular, mean cluster size remains constant with variation in the pressure preceding the nozzle, provided that the temperature in the nozzle varies simultaneously to maintain $p_0T_0^{\gamma(\gamma-1)}$ constant (where γ is the exponent of the adiabatic curve). Similarly, the particle size of the condensed phase remains constant with variation in nozzle diameter if p_0d^q remains constant, where q has the values 0.8 and 0.6 for argon and carbon dioxide respectively. Dimerisation in molecular beams of carbon dioxide takes place[171] only as a result of three-body collisions. The dependence of the concentrations of large clusters (beginning with the trimer) on the pressure in the source and the diameter of the nozzle shows that they may be formed by the combination of single molecules with smaller clusters without the involvement of third bodies. The efficiency of collisions of the monomer with $(CO_2)_x$, where $x = 2–4$, is ~0.03.[172]

It is interesting that Hill and Whitfield[173] observed chemiluminescence in the condensation of nitric oxide, which they attributed to oxidation of a molecule in a cluster to nitrogen dioxide and its detachment in an excited state followed by emission of a photon. The yield of photons is 20% of the number of $(NO)_x + O_2$ collisions. In the Reviewers' opinion this phenomenon indicates that the excitation of an individual molecule in a cluster does not lead to breakdown of the latter; it is of interest in connection with the possible disintegration of clusters on ionisation in the sources of the mass spectrometers normally used for the emission of molecular beams. Becker et al.[174] studied the reflection of nitrogen clusters from a stainless-steel surface. Dissociation of the clusters was not observed on reflection, and the intensity of the beam was almost independent of the temperature of the surface: i.e. the clusters did not absorb energy during the collisions. The beam had greatly narrowed on reflection, since the velocity of the clusters remained constant only parallel to the steel surface. The angles of incidence of the clusters lay in the range 50–75°, and the angles of reflection between 85° and 90° to the normal to the surface. These observations throw a somewhat unexpected light on the character of energy transfer in clusters.

From a study of the formation of a lead aerosol by the decomposition of tetramethyl-lead vapour in a shock tube at 920–960 K Graham and Homer[137] concluded that coagulation is the main factor determining the course of the particle-size distribution in this case. They were able to measure the aerosol coagulation constants, and showed that the decrease in particle concentration with time obeys a $t^{-6/5}$ law, which indicates establishment of a self-sustaining régime of coagulation.

Barschdorf[175] studied the condensation of water vapour in a shock tube in the presence of various carrier gases. He found that, with a mass fraction of the vapour of 0.1, the classic theory underestimates the rate of nucleation, depending on the nature of the carrier gas, by factors of 30–1000. At higher moisture contents the rate of smaller than the calculated value, and for the pure vapour theory overestimates *I* by factors of 10–100. The condensation of the vapours of chloroform and Freons in a shock tube was far more rapid than according to the classic theory.

Isothermal condensation of the vapours of several compounds—alcohols, n-alkanes, esters, and a number of acids—is well described by the classic theory based on the usual surface tension. The rate of nucleation is underestimated, but the discrepancy between theory and experiment can be eliminated by using values of the surface tension found by Band's method[36] from the equation of state of the vapour. For water, sulphuric acid, and certain other compounds theory predicts too low a rate of nucleation at low supersaturations, and too high a value at high supersaturations; no satisfactory explanation has yet been given for this divergence. Nevertheless, the condensation of water has been studied over a wide range of conditions, including non-isothermal conditions with water vapour escaping through a nozzle under various régimes. This permits the use for engineering calculations of formal expressions for the rate of nucleation with empirical corrections.

In the case of the rapid type of nucleation, with a sufficiently long lifetime of the condensing system $t > \theta^* \gg \theta$, the degree of dispersion and the concentration of the condensed phase can readily be calculated by means of known solutions of the coagulation equations, without the need to determine the bonding energy of small clusters or to obtain detailed information on the primary acts of condensation. Results obtained by several workers on these lines permit θ^* and θ to be estimated, and also indicate that θ^* never exceeds $\sim 10^4$. When $t < \theta^*$, the description of rapid condensation requires the above information, which has been successfully accumulated in work using molecular beams.

The theory of non-isothermal nucleation remains in an unsatisfactory position. Most real cases of condensation take place in multicomponent systems. Metastable states of such systems have been subjected to only most general examination[32]. No practical advances in the description of nucleation in multicomponent systems have been made since the early work of Reiss[176,177]. Some little experimental investigation has been made on nucleation in binary mixtures, but not at all in multicomponent systems. It is extremely desirable to develop experimental methods for direct examination of the properties of small clusters and of primary acts in condensation. The only technique used for the latter purpose—molecular beams of high intensity—deals with molecules whose state is far from equilibrium.

Great difficulties are presented by the study of chemical condensation, in which disperse particles arise from chemical reaction in the gas phase. For the present, qualitative and semi-quantitative data are being accumulated on the role of various factors in these complicated processes. The greatest progress has been made in connection with the formation of carbon black[178] and also of photochemical smog[179]. Sufficient attention has not yet been paid to the theoretical study of chemical condensation in other systems, especially in simplified model cases.

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Progress in and Prospects for the Use of Heterocyclic Azo-compounds in Analytical Chemistry

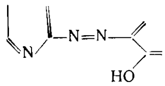
V.M.Ivanov

The effects of substituents in bases and coupling components on the properties of heterocyclic azo-compounds are examined in the pyridine, anabasine, thiazole, quinoline, and antipyrine series and their compounds with metal ions. Methods are indicated for varying the sensitivity of the reagents, the stability of the resulting complexes, and the selectivity of reactions with inorganic ions. Prospects for the use of heterocyclic azo-compounds in analytical chemistry are noted. A list of 199 references is included.

CONTENTS

I. INTRODUCTION

Heterocyclic azo-compounds include reagents containing the atomic grouping



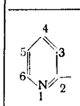
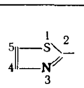
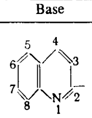
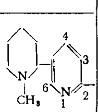
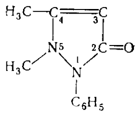
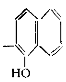
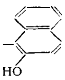
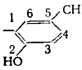
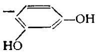
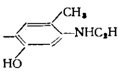
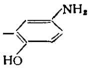
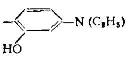
The bases used are amines of nitrogenous heterocycles (pyridine, thiazole, benzothiazole, quinoline, pyrimidine, anabasine, antipyrine, and other derivatives), and the coupling components are aromatic hydroxy-compounds (phenol, resorcinol, naphthol, quinolinol, etc.). The number of papers on heterocyclic azo-compounds and their analytical applications increases annually, having reached around 150, 400, 700, and above 1100 by 1964, 1968, 1972, and the end of 1975 respectively. Such compounds are widely used as reagents for photometric and extraction–photometric determinations, as complexometric indicators, and as indicators in the determination of various anions by precipitation[1–4]. They form with many metal ions intensely coloured compounds, the complexing reactions exhibiting high contrast, which underlies many methods for determining inorganic ions by their use.

Most of the publications have been devoted to the practical application of heterocyclic azo-compounds in the analysis of naturally and industrially occurring substances, and very few studies have been concerned with elucidating the reasons for the great reactivity of these reagents, examining the effect of substituents on the properties of reagents and complexes, and other theoretical aspects.

The present Review deals only with the optical characteristics of the complexes, since, as noted above, the ability to form coloured complexes with metal ions underlies methods for determining the latter. Table 1 lists structural formulae and the abbreviations for the reagents adopted in the literature.

The following symbols are used in the Review: ϵ is the molar extinction coefficient, β the overall stability constant of the complex, K_{eq} the equilibrium constant of complex formation, K_{OH} the dissociation constant of the hydroxy-group *ortho* to the azo-group, K_{NH} the dissociation constant of the protonated heterocyclic nitrogen atom *ortho* to the azo-group, E the dielectric constant of the solution, and μ the ionic strength of the solution.

Table 1. Structural formulae and abbreviations for heterocyclic azo-compounds.

Coupling component	Base				
	 pyridine	 thiazole	 quinoline	 methylanabasine	 antipyrine
	1-PAN	1-TAN	1-(2-QAN)	1-MAN	1-ANAN
	2-PAN	2-TAN	2-(2-QAN)	2-MAN	2-ANAN
	*o*-PAC	*o*-TAC	–	–	–
	PAR	TAR	2-QAR	MAAR	ANAR
	PAAC	TAAC	2-QAAC	MAAC	ANAC
	–	–	–	MAAP I	–
	PAAP	TAAP	2-QAAP	MAAP II	ANAP

The value of photometric organic reagents is determined by the totality of properties of reagents and complexes—the sensitivity and selectivity of the reagent, the degree of contrast in the colour change of the solution on complex formation, the stability of the complexes formed—properties which will be surveyed below.

II. SENSITIVITY OF HETEROCYCLIC AZO-COMPOUNDS

The sensitivity of reagents in photometric analysis is expressed by the limiting dilution or the detectable minimum. Increasing use has been made during recent years of the molar extinction coefficient as the most objective characteristic of the sensitivity: from its value together with the sensitivity of the instrument, the minimum determinable optical density, the volume of the solution, and the thickness of the absorbing layer we can calculate the limiting dilution or the detectable minimum. The extinction coefficient ϵ is used in the present Review as a measure of the sensitivity of a reagent.

Role of Base

Azo-compounds derived from pyridine are usually the most sensitive. They are followed by anabasine, quinolin-2-amine, thiazole, and finally antipyrine derivatives. This rule is confirmed with reagents formed with resorcinol (Table 2), ethylamino-*p*-cresol, and *m*-diethylaminophenol, and is valid for the majority of ions. However, not only the nature of the heterocycle but also the position of the amino-group relative to the heterocyclic atom is significant. Reagents based on quinolin-2-amine are more sensitive than those based on quinoline-8-amine. Thus $10^{-4}\epsilon$ has the values 7.1 and 6.0 for the compounds of cobalt(II) with 2-QAAC and 8-QAAC respectively; the corresponding values for the gallium compounds are 9.8 and 7.4, and with 2- and 8-QAAT 10.5 and 7.7.[17,18] Derivatives of quinolin-2-amine are preferable to those of the 8-isomer also for copper and indium.

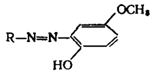
Table 2. Effect of base on sensitivity of determination of ions (resorcinol derivatives)*.

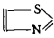
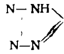
Reagent	$10^{-4}\epsilon$				
	Cu^{II}	Ga^{III}	In^{III}	Ni^{II}	Co^{II}
PAR	5.9[5]	9.9[6]	3.3[7]	7.3[8]	6.0[9]
TAR	3.1[10]	6.3[11]	2.3[12]	6.6[13]	5.6[9]
2-QAR	4.9[14]	4.7[14]	6.0[14]	5.5[14]	6.6[14]
MAAR	5.4[15]	—	3.8[16]	—	—

* Complexes having a dissociated *p*-hydroxy-group are compared.

The sensitivity of a reagent is little affected by increase in the number of heteroatoms in the base, provided that the latter does not contain fused rings. Indeed, reagents derived from pyridine and from thiazole are closely similar in sensitivity, although introduction of the new heteroatom (sulphur) may change the reactivity of the reagents and the mechanism of complex formation. The optical characteristics of the reagents change significantly. The introduction of fresh heteroatoms, e.g. nitrogen, has a substantial effect on the properties and the ionic form of the reagent, the absorption maxima and intensity, and the dissociation constants (Table 3). The properties of the complexes are also changed: for the copper compounds of TAMP, TRAMP, and TEAMP, for example, the light-absorption maxima occur respectively at 631, 578, and 578 nm, the logarithms of the stability constants are 9.8, 16.28, and 10.56, and the sensitivity ($10^{-4}\epsilon$) is practically the same (0.71 and 0.84 for the TRAMP and TEAMP compounds)[19].

Table 3. Effect of number of heterocylic nitrogen atoms on properties of reagents[19] (2 vol.% ethanol).



Reagent (R)	Form	λ_{max}, nm	$10^{-4}\epsilon$	pK_n
TAMP 	H_2R^+ HR R^-	523 468 561	1.4 1.2 1.4	—0.03±0.03 8.13±0.02
TRAMP 	H_3R^{2+} H_2R^+ HR R^-	470 432 520—550 494	0.6 0.5 0.5 1.1	—0.10±0.02 7.79±0.05 9.69±0.04
TEAMP 	H_3R^{2+} H_2R^+ HR R^-	468—480 460 422 503	1.4 5.3 5.4 9.2	—2.81±0.05 3.37±0.06 8.69±0.06

A similar rule is observed with the six-membered pyridine and pyrimidine heterocycles: thus the zinc(II), copper(II), and nickel(II) compounds of 2-pyrid-2′-ylazo-1-naphthol (1-PAN) have sensitivities ($10^{-4}\epsilon$) of respectively 2.5, 2.1, and 2.2,[20] while the corresponding 2-pyrimidin-2′-ylazo-1-naphthol (1-PAN) compounds have 2.5, 2.0, and 2.1.[21] The absorption maxima of the two series of complexes are slightly displaced (by 2–4 nm).

Hence the sensitivity of heterocyclic azo-compounds towards metal ions should be enhanced primarily not by changing the nature of the base but by a different procedure, e.g. by introducing substituents at certain positions. Monatomic substituents having a high Coulombic integral, e.g. chlorine or bromine, may have a significant influence on the sensitivity of reagents when located at position 5 in the pyridine ring[22–25]. Reagents containing bromine are usually more sensitive than those with chlorine at this position (Tables 4 and 5).

Table 4. Comparative sensitivity of 2-Pan and its halogenated derivatives.

Ион	2-PAN (Ref.26)		5′-Cl-PAN (Ref.26)		5′-Br-PAN (Ref.27)	
	λ_{max}, nm	$10^{-4}\epsilon$	λ_{max}, nm	$10^{-4}\epsilon$	λ_{max}, nm	$10^{-4}\epsilon$
Mn^{II}	562	4.8	566	7.2	574	7.2
Ni^{II}	570	5.0	580	7—8	582	8—9
Cu^{II}	564	4.4	567	5.8	572	5.2
Zn^{II}	550	5.6	569	7.1	570	6.7
Pd^{II}	678	1.9	670	0.8	695	1.8
Cd^{II}	555	4.9	560	7.0	568	7.3

The effect of a methyl group can be traced only on a few complexes. For example, the sensitivity of resorcinol reagents towards indium is enhanced by the introduction of methyl: values of $10^{-4}\epsilon$ for the compounds with PAR and 4′-6′-CH_3-PAR are respectively 3.3, 4.5, 3.9, and 4.3; the bromo-derivative is more sensitive (5.6 for 5′-Br-PAR)[7,14]. Towards copper(II), cobalt(II), nickel(II), zinc(II), and uranium(VI) PAR is more sensitive than its analogues containing methyl in the pyridine ring[43]: the sensitivity towards these ions diminishes in the sequence PAR > 4′-CH_3-PAR > 5′-CH_3-PAR > 6′-CH_3-PAR. Methylation of the pyridine or thiazole ring is evidently undesirable, since in most cases it lowers the sensitivity of the reagents (Table 6). The enhancement of sensitivity towards indium can be explained by the formation of compounds having the proportions M : R = 1 : 3 in the case of the methylated derivatives, but 1 : 1 compounds when indium reacts with PAR. The diminished sensitivity in the case of 3′-CH_3-PAR was attributed[43] to steric hindrance due to rotation of the hydroxy-group in the coupling component to the *trans*-position relative to the 3-substituent in the base. If this is true, any 3-substituent in the base, especially a bulky substituent, should diminish the sensitivity of the reagent. This rule applies to most ions (Table 7). Dibromo-derivatives are almost always less sensitive than the monobromo-derivatives, although in several cases more sensitive than the unbrominated reagents.

Table 5. Effect of halogenation of base on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$					
	Co^{II}	Cu^{II}	Pd^{II}	Ga^{III}	In^{III}	Tl^{III}
2-PAN	3.0[28]	4.4[27]	1.4[27]	2.2[29]	1.9[7]	2.2[30]
5′-Br-PAN	4.1[31]	5.2[27]	1.8[27]	—	1.1[27]	—
PAAC	7.4[32]	3.8[33]	2.8[34]	11.9[35]	2.9[36]	5.5[37]
5′-Br-PAAC	7.5[32]	5.4[33]	4.0[34]	11.5[35]	5.0[38]	8.6[25]
PAAP	8.6[39]	3.8[24]	4.7[40]	9.6[41]	7.5[42]	6.6[25]
5′-Br-PAAP	9.8[39]	6.2[24]	4.3[40]	12.3[41]	7.8[42]	11.9[25]

Table 6. Effect of methylation of base on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$				
	Cu^{II}	Ni^{II}	Co^{II}	Ga^{III}	In^{III}
PAR	5.9[5]	7.1[44]	6.0[9]	9.9[6]	3.3[7]
6′-CH_3-PAR	4.7[14]	5.1[14]	5.4[14]	4.2[14]	4.3[14]
TAR	3.1[10]	6.6[13]	5.6[9]	6.3[11]	—
4′-CH_3-TAR	2.4[45]	—	3.8[46]	—	—
TAAC	3.7[45]	—	5.8[46]	6.5[47]	3.7[23]
4′-CH_3-TAAC	3.1[45]	—	—	—	2.5[23]

Table 7. Effect of bromination on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$								
	V^{V}	Co^{II}	Cu^{II}	Ga^{III}	Nb^{V}	Pd^{II}	In^{III}	Tl^{III}	Bi^{III}
PAR	3.6[48]	6.0[9]	5.9[5]	10.2[49]	3.5[50]	1.8[51]	3.3[7]	2.9[12]	1.1[5]
5′-Br-PAR	—	5.6[9]	—	—	2.1[52]	—	5.6[7]	—	—
3′,5′-Di-Br-PAR	—	2.4[9]	—	—	1.6[52]	—	—	—	—
PAAC	3.8[53]	7.4[32]	3.8[33]	11.9[35]	3.9[54]	2.8[34]	2.9[36]	5.1[37]	4.4[55]
5′-Br-PAAC	3.7[53]	7.5[32]	5.4[33]	11.5[35]	3.5[50]	4.0[34]	5.0[38]	8.6[25]	4.6[56]
3′,5′-Di-Br-PAAC	4.1[53]	6.0[32]	4.7[33]	10.4[35]	2.3[50]	3.5[43]	4.3[38]	5.2[37]	5.2[56]
PAAP	6.0[13]	8.6[39]	3.8[24]	9.6[57]	3.6[50]	4.7[40]	7.5[42]	6.6[58]	3.8[56]
5′-Br-PAAP	4.0[13]	9.8[39]	6.2[24]	12.3[41]	3.0[52]	4.3[40]	7.8[42]	11.9[25]	5.8[56]
3′,5′-Di-Br-PAAP	5.0[13]	9.3[39]	5.9[24]	8.8[41]	2.0[52]	4.1[40]	5.0[42]	9.2[25]	6.6[56]

A sulpho-group is usually introduced to increase the solubility of the reagent and of the complex. It has little effect on the sensitivity of the reagent or the degree of contrast of the reaction. For example, values of $10^{-4}\epsilon$ for compounds of palladium with TAR, TAR-5′-sulphonic acid, 2,4-dihydroxy-5-thiazol-2′-ylazobenzoic acid, and its 5′-sulpho-derivative are respectively 0.93, 0.93, 0.82, and 0.69.[59,60]

From the above effects of substituents it may be concluded that reagents based on 5-bromopyridin-2-amine should be the most sensitive.

Role of Coupling Component

It was shown[22,23] by a quantum-chemical method that substituents introduced *para* to the azo-group into the coupling component may change significantly the sensitivity of the reagents: the more polarisable the substituent, the more sensitive the reagent. The sensitivity should thus increase in the sequence of reagents containing the substituent

phenol < naphthol < resorcinol < ethylamino-*p*-cresol < diethylaminophenol

Naphthol derivatives are used most often, but the general rule is not observed with azonaphthols based on pyridine and anabasine. Among pyridylazonaphthols, for example, 1-PAN is more sensitive than is 2-PAN: the corresponding values of $10^{-4}\epsilon$ for the nickel(II) compounds are 2.2 and 1.9,[20] for cobalt(III) compounds 3.3 and 2.5,[27,31] cobalt(II) 3.9 and 3.0,[28,31] copper(II) 4.8 and 4.4,[27,61] zinc(II) 6.6 and 5.8,[62,63] and thallium(III) compounds 3.9 and 2.2.[30,63] With anabasine, 2-naphthol derivatives are the more sensitive: values of $10^{-4}\epsilon$ for the copper(II) compounds of 1-MAN and 2-MAN and respectively 2.2 and 3.0;[15] the corresponding values for the cobalt(II) compounds are 1.0 and 1.9.[65,66] The influence of the substitution in the coupling component on the sensitivity of the reagents is shown in Tables 8 and 9.

Table 8. Effect of coupling component on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$				Reagent	$10^{-4}\epsilon$			
	V^{V}	Co^{II}	Nb^{V}	Cu^{II}		V^{V}	Co^{II}	Nb^{V}	Cu^{II}
o-PAC	0.7[53]	1.5[32]	0.6[52]	0.9[67]	PAAP	6.0[53]	8.6[39]	3.8[52]	3.8[24]
2-PAN	1.7[27]	3.0[28]	—	4.4[27]	TAR	2.7[68]	5.6[9]	3.2[69]	3.1[10]
PAR	3.6[48]	6.0[9]	3.5[50]	5.9[5]	TAAC	2.8[53]	5.8[46]	3.6[70]	—
PAAC	3.8[53]	7.4[32]	3.9[54]	3.8[33]	TAAP	3.5[71]	7.0[39]	3.5[70]	—

Table 9. Molar extinction coefficients of compounds of azo-derivatives of anabasine with metal ions.

Reagent	$10^{-4}\epsilon$				Reagent	$10^{-4}\epsilon$			
	Mn^{II}	Cu^{II}	Co^{II}	In^{III}		Mn^{II}	Cu^{II}	Co^{II}	In^{III}
1-MAN	3.8[72]	2.2[15]	0.8[73]	1.9[74]	MAAP I	7.6[72]	4.1[15]	—	—
MAAR	6.1[72]	5.4[15]	—	3.8[16]	MAAP II	11.2[72]	5.6[75]	7.8[75]	6.1[75]

Resorcinol derivatives, able to form two types of complexes, occupy a special position. In acid medium the *para*-hydroxyl does not dissociate, and *protonated* complexes (MRH) are formed. The degree of contrast in the change in colour on complex formation is very great, especially with complexes of cobalt(II) and the platinum metals; the sensitivity of the reagents is close to that of azo-derivatives of phenol. In neutral medium the *para*-hydroxyl begins to dissociate, which is equivalent to introduction of an auxochrome into the reagent molecule. The complexes formed have been termed *normal* (MR), and are intensely coloured (Table 10); they are extracted only by polar solvents such as alcohols. The conversion of protonated into normal complexes is reversible and very rapid. The former may find application in analytical chemistry, despite the weakness of their colour. They are formed only by certain metal ions, and in acid medium, where interaction of these ions with heterocyclic azo-compounds is highly selective, the complexes are readily extracted by non-polar solvents. After selective extraction they can be re-extracted by a buffer solution as normal complexes having high molar extinction coefficients.

Table 10. Molar extinction coefficients of protonated and normal complexes (MRH and MR).

Reagent	Ion	$10^{-4}\epsilon$		Reagent	Ion	$10^{-4}\epsilon$	
		MRH	MR			MRH	MR
PAR	U^{VI}(Ref.76)	1.9	3.8	TAR	U^{VI}(Ref.81)	2.4	3.4
	Pd^{II}(Ref.77)	1.5	1.8		Pd^{II}(Ref.59)	0.9	2.2
	Rh^{III}(Ref.78)	0.9	2.7		Rh^{III}(Ref.82)	0.6	2.5
	Pt^{II}(Ref.79)	2.3	6.0		Cu^{II}(Ref.10)	1.9	3.1
	Pr^{III}(Ref.80)	1.1	2.0		Bi^{III}(Ref.10)	2.2	3.1
	Nd^{III}(Ref.80)	1.1	4.0		Pb^{II}(Ref.10)	2.0	3.0
	Er^{III}(Ref.80)	1.6	4.1		Zn^{II}(Ref.10)	3.1	3.5

The effect of dissociation of the *para*-hydroxyl on the sensitivity of reagents has been demonstrated convincingly. If this group is methylated, the sensitivity of the reagents is greatly decreased, although the degree of contrast of the reaction is not appreciably affected (Table 11).

Table 11. Molar extinction coefficients of compounds with thiazolylazoresorcinol and its methyl ethers.

Ion	$10^{-4}\epsilon$ for compounds with the reagent*		
	TAR	TAMR (Ref.83)	TAMG (Ref.83)
Cu^{II}	3.1 (505)[10]	3.1 (535)	1.3 (631)
Cd^{II}	3.2 (500)[10]	2.8 (508)	1.5 (598)
Hg^{II}	—	2.8 (537)	1.4 (628)
Zn^{II}	3.5 (500)[10]	2.7 (513)	1.6 (594)
Ni^{II}	6.6 (510)[13]	3.1 (520)	1.5 (608)
Co^{II}	5.6 (510)[9]	2.8 (511)	0.9 (618)
U^{VI}	3.4 (540)[81]	2.0 (530)[84]	1.4 (610)[84]

* Absorption maxima (nm) indicated in parentheses.

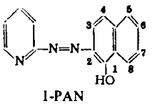
Both the coupling component and the base contain positions (e.g. 6) at which the sensitivity of the reagents is greatly diminished by substituents. Indeed, the reagent becomes much less sensitive, although the degree of constrast of the reactions changes just as greatly (Table 11). The marked decrease in sensitivity can be attributed to steric hindrance due to possible rotation of the *ortho*-hydroxyl to the *trans*-position with respect to the heterocyclic nitrogen atom. This also explains why *p*-cresol derivatives are the least sensitive reagents of all those listed in Table 8. The size of the substituent has different effects in azo-derivatives of pyridine and of thiazole, as is shown by Table 12 for compounds of uranium(VI) with PAR, TAR, and their derivatives[84].

Table 12.

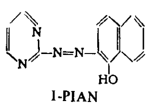
Reagent	PAR	6′-CH_3-PAR	6′-C_2H_5-PAR	6′-C_3H_7-PAR	TAR	6′-CH_3-TAP	6′-C_2H_5-TAR
$10^{-4}\epsilon$	3.8	3.6	1.3	1.7	3.2	3.0	2.9

The introduction of substituents into bases and coupling components at positions giving rise to steric hindrance on complex formation produces a sharp decrease in the molar extinction coefficient. For compounds of cobalt(II) with PAR, 5′-Br-PAR, 4-(3,5-dibromopyrid-2-ylazo)resorcinol, 2,6-dibromo-4-pyrid-2′-ylazoresorcinol, and 2,6-dibromo-4-(3,5-dibromopyrid-2-ylazo)resorcinol, for example, values of $10^{-4}\epsilon$ are respectively 6.0, 5.6, 2.4, 5.2, and 3.0.[9]

Table 13. Effect of sulphonation of naphthalene ring on properties of compounds of reagents with metal ions.



1-PAN



1-PIAN

Reagent	pK^*_{NH}	pK^*_{OH}	Zn^{II}		Cu^{II}		Ni^{II}		Pd^{II}	
			λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$
1-PAN (Ref.20)	2.29	10.00	545	2.5	566	2.1	548	2.2	—	—
1-PAN-4-SO_3H	2.03	8.63	528	2.6	555	2.3	563	4.2	650	1.2
1-PAN-5-SO_3H	2.39	9.11	543	2.3	567	2.3	580	4.1	631	0.9
1-PAN-6-SO_3H	2.48	9.13	545	2.5	570	2.2	582	4.3	675	0.9
1-PAN-7-SO_3H	2.46	9.09	543	2.6	569	2.2	579	4.2	670	1.0
1-PAN-8-SO_3H	2.85	10.44	589	2.7	582	2.2	592	4.3	703	1.3
1-PIAN (Ref.21)	0.92	9.66	543	2.5	564	2.0	544	2.1	—	—
1-PIAN-4-SO_3H	0.58	8.41	529	2.7	555	2.2	572	4.1	670	1.1
1-PIAN-5-SO_3H	0.87	8.87	541	2.7	565	2.2	583	3.9	690	1.0
1-PIAN-6-SO_3H	0.89	8.91	544	2.7	569	2.3	583	4.1	696	1.0
1-PIAN-7-SO_3H	0.87	8.66	542	2.7	567	2.2	585	3.9	693	1.0
1-PIAN-8-SO_3H	1.17	10.10	551	2.7	576	2.1	582	3.5	710	1.1

*μ = 0.1; 50 vol.% CH_3OH.

Sulphonation of the coupling component has hardly any effect on the sensitivity of the reagents, but influences the acid–base properties of the ligands (Table 13). Reactions showing the greatest and smallest contrast are obtained with a sulpho-group at positions 8 and 4 respectively. The sharp increase in sensitivity of the sulphonic acids towards nickel was attributed[20, 21] to the formation of compounds having Ni : R = 1 : 2, whereas 1-PAN and 1-PIAN yield 1 : 1 compounds. The interesting rule was established[20] that the bathochromic shift on passing from the protonated form H_2R^+ to the completely dissociated R^- is proportional to the overall

$$H_2R^+ \rightleftarrows 2H^+ + R^-$$

dissociation constant for 1-PAN, 2-PAN, and the sulphonated derivatives. This rule probably applies to other reagents, as the Reviewer has established for 1-PIAN and its sulphonic acids—data taken from Ref. 21 (Fig. 1 and Table 14).

Table 14. Absorption maxima and ionisation constants of PAN, PIAN, and their sulphonic acids.

Reagent	λ, nm		ν, cm^{-1}		Δν, cm^{-1}	pK_{NH}	pK_{OH}	pK_{NH} + + pK_{OH}
	H_2R^+	R^-	H_2R^+	R^-				
2-PAN	425	495	23 530	20 200	3330	2.32	12.00	14.32
1-PAN	460	514	21 740	19 460	2280	2.29	10.00	12.29
1-PAN-4-SO_3H	465	498	21 510	20 080	1430	2.03	8.63	10.66
1-PAN-5-SO_3H	463	510	21 600	19 610	1990	2.39	9.11	11.50
1-PAN-6-SO_3H	465	513	21 510	19 490	2020	2.48	9.13	11.61
1-PAN-7-SO_3H	465	512	21 510	19 530	1980	2.46	9.09	11.54
1-PAN-8-SO_3H	468	532	21 370	18 800	2570	2.85	10.44	13 29
1-PIAN	455	523	21 980	19 120	2860	0.92	9.66	10.58
1-PIAN-4-SO_3H	445	508	22 470	19 690	2780	0.58	8.41	8.99
1-PIAN-5-SO_3H	447	523	22 370	19 120	3250	0.87	8.87	9.74
1-PIAN-6-SO_3H	452	527	22 120	18 980	3240	0.89	8.91	9.80
1-PIAN-7-SO_3H	449	523	22 270	19 120	3150	0.87	8.66	9.53
1-PIAN-8-SO_3H	448	531	22 320	18 830	3490	1.17	10.10	11.27

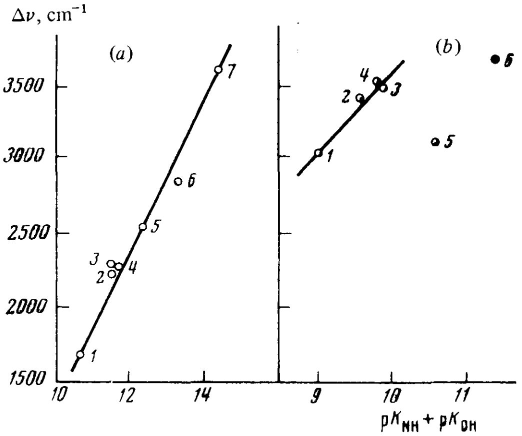


Figure 1. Effect of basicity of ligand on bathochromic shift in the reaction $RH_2^+ \rightleftharpoons R^- + 2H^+$ for: (*a*) pyridylazonaphthols[20]: *1*) 1-PAN-4-SO_3H; *2*) 1-PAN-5-SO_3H; *3*) 1-PAN-6-SO_3H; *4*) 1-PAN-7-SO_3H; *5*) 1-PAN; *6*) 1-PAN-8-SO_3H; *7*) 2-PAN; (*b*) pyrimidinylazonaphthols[21]: *1*) 1-PIAN-4-SO_3H; *2*) 1-PIAN-7-SO_3H; *3*) 1-PIAN-6-SO_3H; *4*) 1-PIAN-5-SO_3H; *5*) 1-PIAN; *6*) 1-PIAN-8-SO_3H.

Extraction enables the sensitivity of the reagent to be improved by concentrating the element. Little attention has hitherto been paid to the influence of the dielectric constant of the solution, which can be varied by suitable choice of solvent and the use of solvent mixtures. With aqueous-organic and organic-solvent solutions the molar extinction coefficients can also be changed. For example, among the solvents studied—tetrachloromethane, chloroform, benzene, diethyl and di-isopropyl ethers, and 4-methylpentan-2-one—the sensitivity for the determination of zinc[85] and cadmium[86] by means of 5′-Cl-2-PAN is greatest in diethyl-ether solution ($10^{-4}\epsilon$ = 8.5 and 6.6 for the respective metals) and least in di-isopropyl ether (5.1 and 5.4). The degree of contrast of the reactions remains almost unchanged (Table 15).

An advantage of heterocyclic azo-compounds is the great contrast of the change in colour of the solution on complex formation. This is responsible for their widespread use as complexometric indicators. Reactions with such compounds based on cresol derivatives and the reactions of almost all the reagents with cobalt(III) and the platinum metals exhibit especially high degrees of contrast: the absorption of light by the reagents at the absorption maximum of the complex is almost zero, while this maximum for the complex is displaced 200 nm or more relative to the absorption maximum of the reagents under the same conditions.

Table 15. Molar extinction coefficients of cobalt(II) compounds of heterocyclic azo-compounds in various solvents[31].

Solvent	Absorption max. (nm) (and molar extinction coefficients, $10^{-4}\epsilon$) of Co^{II} complexes of the reagents				
	2-PAN	Cl-PAN	Br-PAN	TAN	Br-TAN
CCl_4	2.7 (500)	2.4 (535)	3.1 (540)	3.2 (550)	4.8 (570)
$CHCl_3$	3.0 (525)	3.1 (535)	4.1 (540)	3.3 (555)	4.7 (570)
C_6H_6	3.5 (530)	2.7 (535)	4.0 (540)	3.4 (550)	5.3 (570)
$(C_2H_5)_2O$	3.2 (520)	— —	4.4 (540)	3.3 (550)	4.2 (560)
n-$C_5H_{11}OH$	2 7 (520)	2.9 (535)	4.6 (540)	3.3 (550)	— —

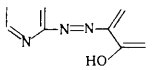
Table 16. Degrees of contrast of reactions of PAAC, PAAP, and their derivatives with metal ions.

Reagent	Ga^{III} (Reg.17)		Cu^{II} (Ref.24)		Nb^{V} (Ref.52)	
	Δλ, nm	ϵ_c/ϵ_r	Δλ, nm	ϵ_c/ϵ_r	Δλ, nm	ϵ_c/ϵ_r
PAAC	100	91.0	105	2.7	145	41
5-Br-PAAC	110	100.0	105	14.9	145	31
3,5-Di-Br-PAAC	115	94.5	105	4.9	140	20
PAAP	110	46.0	100	5.9	145	38
5-Br-PAAP	125	137.0	115	6.4	140	27
3,5-Di-Br-PAAP	120	52.0	110	7.3	145	17

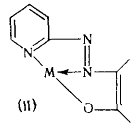
Improvement by monohalogenation of the analytical properties of the most promising reagents—PAAC and PAAP—increases the degree of contrast of complex formation as a consequence of a bathochromic shift; often the ratio of the molar extinction coefficients of complex and reagent ϵ_c/ϵ_r at the absorption maximum of the former becomes larger, the molar extinction coefficient of the compound with the monohalogenated reagent increasing considerably in comparison with the corresponding value of the unhalogenated reagent. Use of these reagents in photometric analysis is restricted by the poor sensitivity of azo-derivatives of *p*-cresol, despite the high degree of contrast of the reaction (Table 16).

III. STABILITY OF COMPLEX COMPOUNDS

Stability is an important characteristic of a complex compound, since the stability constants of the complexes and the acid dissociation constants of the ligands enable optimum conditions to be calculated for determining an inorganic ion and making its reaction with the chosen ligand as selective as possible. The stability of a complex compound depends on the denticity of the ligand, the basicity of the donor atoms in it, the acid-base properties of the functional group involved in complex formation, the coordination number and the ionic radius of the central ion, the number and size of the rings formed, the molar proportions in which the components interact, and other factors.



(I)



(II)

Most investigators regard heterocyclic azo-compounds as terdentate ligands. The atomic grouping (I) is involved in complex formation, and yields two rings (II) on interaction with one ligand. Of the two nitrogen atoms forming the azo-group that which is farther from the heteroatom of the base is the more reactive.

The multidenticity of heterocyclic azo-compounds as ligands explains that great stability of the complexes formed. Elimination of one of the atoms from the grouping (I) and its replacement by a carbon atom have marked effects on the stability of the complexes. For example, values of lg β_1 for the compounds of copper with PAR, 2-PAN, 4-phenylazoresorcinol (replacement of heterocyclic nitrogen atom by a carbon atom), *o*-pyrid-2ʹ-ylmethylenaminophenol (azo-group replaced by CH : N), *o*-pyrid-2ʹ-yliminomethylphenol (azo-group replaced by N : CH), and *NN*-dimethyl-4-pyrid-2ʹ-ylazoaniline (hydroxy-group eliminated from coupling component) are respectively 16.4, 16.0, 13.9, 13.8, 7.3, and 5.2.[2]

Basicity of Ligand

The basicity of the heterocycle decreases in the sequence of heterocyclic amines (values of pK_a given in parentheses) 2-aminoquinoline (7.34) > 2-aminopyridine (6.86) > 2-aminothiazole (5.39) > 2-aminobenzothiazole (4.51) > 8-aminoquinoline (3.99) > 2-aminopyrimidine (3.54).[87]

Table 17. Dissociation constants (pK_{OH}) of heterocyclic azo-compounds.

Reagent	Conditions	pK_{OH}	Ref.
4-Thiazol-2ʹ-ylazoresorcinol	2 vol.% C_2H_5OH, $\mu = 0.1$	9.44	10
3-Thiazol-2ʹ-ylazopyridine-2,6-diol	8 vol.% C_2H_5OH, $\mu = 0.1$	5.83	88
2-Quinol-2ʹ-ylazo-1-naphthol	50 vol.% dioxan	10.65	89
7-Quinol-2ʹ-ylazoquinolin-8-ol	$\mu = 0.1$	8.30	90
2-Benzothiazol-2ʹ-ylazo-1-naphthol	isopentanol	7.90	91
7-Benzothiazol-2ʹ-ylazoquinolin-8-ol	10 vol.% C_2H_5OH, $\mu = 0.01$	7.22	9[?92]
2-Pyrid-2ʹ-ylazo-1-naphthol	20 vol.% C_2H_5OH, $\mu = 0.5$	11.11	61
7-Pyrid-2ʹ-ylazoquinolin-8-ol	4 vol.% C_2H_5OH, $\mu = 0.4$	7.90	93

The introduction of a heterocyclic nitrogen or sulphur atom, having a lone pair of electrons not involved in the general chain of conjugation, is equivalent to introducing a strongly negative substituent such as a nitro-group. The acidic properties of such ligands should be intensified, and the stability of the resulting complexes diminished. If a heteroatom is introduced also into the coupling component, the acidity of the hydroxyl *ortho* to the azo-group is strengthened, and to a greater extent the closer is the heteroatom (resorcinol and pyridinediol, naphthalene and quinolinol azo-derivatives—Table 17).

Influence of Solvent

The widespread use of organic reagents in analytical chemistry poses the problem of studying the effect of solvents on the acid–base properties of ligands and the stability of complexes. If the reagent is present in protonated form (with the heteroatom protonated) in solution, its dissociation constant will increase with decrease in the dielectric constant of the solution; but if it is present in molecular or anionic form, it will become less acidic with decrease in the dielectric constant. This rule holds for 1-(2-QAN),[89] PAN and TAN,[94] PAR and TAR,[95] TAMR,[96] methyl 2-3ʹ,4ʹ-dihydroxyphenylazo-4-hydroxymethylthiazole-5-carboxylate[97], and 4-thiazole-2ʹ-ylazocatechol[98]. For PAN and TAN, independently of the nature of the solvent (dioxan, ethanol, acetone, dimethylformamide) at concentrations of 20–50 vol.%, a single equation can be deduced[94] relating the conventional dissociation constant of the reagent with the dielectric constant of the solution (Table 18).

Table 18.

for PAN $\mathrm{p}K_{NH} = 1.12 + 0.0175E - A\ (E = 35 - 75)$,
$\mathrm{p}K_{OH} = 14.07 - 0.0260E - A\ (E = 50 - 75)$;
for TAN $\mathrm{p}K_{NH} = 0.47 + 0.0235E - A\ (E = 45 - 70)$,
$\mathrm{p}K_{OH} = 10.43 - 0.0215E - A\ (E = 50 - 70)$,

where $A = \dfrac{\sqrt{\mu}}{1 + \sqrt{\mu}}\ (\mu = 0.1 - 0.5)$.

Table 19. Effect of dioxan on ionisation constants of 1(2-1-(2-QAN) and its copper and zinc complexes (μ = 0.1).[89]

Dioxan, vol.%	Reagent		Copper complex	Zinc complex	
	pK_{NH}	pK_{OH}	lg β_2	lg β_1	lg β_2
30	2.65	10.03	12.74	—	—
34	2.59	10.16	12.85	—	—
40	2.33	10.35	13.04	—	—
44	—	—	13.20	9.73	—
50	2.03	10.65	13.35	9.88	20.25
54	—	—	—	9.97	20.34
60	—	—	—	10.13	20.29

This rule must be taken into account when the selectivity of determination is to be enhanced. With decrease in dielectric constant of the solution the ligand should interact with the test ion in a more acid medium because of the more acidic properties of the protonated heteroatom, while the complex should become more stable as a result of the increased basicity of the hydroxy-group (Table 19).

Molar Ratio of Components and Scheme of Complex Formation

The example of a single ligand, 2-PAN, can be used to show the variety of types of complexes formed with ions of different metals[99]: MR_2^0 with manganese, cadmium, nickel, and uranium(VI); MR_2^+ with iron(III), yttrium, indium, and cobalt(III); MR^{2+} with gallium and thallium(III); MR^0 with vanadium(V); and MR^+ with palladium(II) and copper(II). Complexes having M : R = 1 : 2 are in all cases more stable than the 1 : 1 complexes: for zinc(II) lg β_1 = 12.3 and lg β_2 = 21.7, nickel(II) 14.0 and 27.5, manganese(II) 8.5 and 16.4,[100] and copper(II) 16.2 and 30.5.[101] Highly coordinated complexes are especially stable: for example, lg β_{1-4} for the europium(III) complexes with 2-PAN have the values 12.4, 23.8, 34.5, and 43.7; the corresponding values for the holmium(III) complexes are 12.7, 24.4, 34.8, and 44.1; and for the complexes of ytterbium(III) with 2-TAN 9.8, 19.3, 28.5, and 37.4.[101,102]

Table 20.

$H_3R^+ + Pt(II) \rightleftarrows PtRH + 2H^+$	PAR	pH 1.6—2.1
$PtRH \rightleftarrows PtR + H^+$	PAR	pH 3.9—4.5
$\begin{cases} HR + Pt(II) \rightleftarrows PtR + H^+ \\ H_2R^+ \rightleftarrows HR + H^+ \end{cases}$	PAN	pH 0.5—3.1
	5-Br-PAAP	pH 2.0—3.2
$H_2R^+ + Pt(II) \rightleftarrows PtR + 2H^+$	PAAC	pH 0.5—2.0
	PAAP	pH 0.2—1.6
	5-Br-PAAP	pH — 0.1—1.2

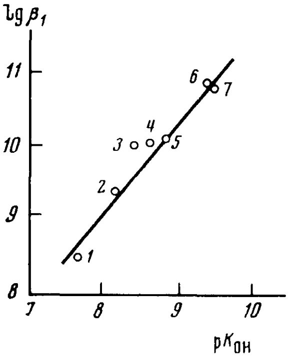


Figure 2. Effect of basicity of ligand[104] on stability of copper compounds[105] (1 : 1 complexes; spectrophotometric determination in presence of 20 vol.% of dioxan) of: 1) 4-chloro-2-thiazol-2′-ylazophenol; *2*) 4-methyl-2-4′-methylthiazol-2′-ylazophenol; *3*) 4-methoxy-2-thiazol-2′-ylazophenol; *4*) 4-methoxy-2-4′-methylthiazol-2′-ylazophenol; *5*) 4-methyl-2-thiazol-2′-ylazophenol; *6*) 2,4-dimethyl-6-4′-methylthiazol-2′-ylazophenol; *7*) 2,4-dimethyl-6-thiazol-2′-ylazophenol.

The diversity of the schemes of complex formation with azo-compounds of the pyridine series can be shown with platinum(II) as example (Table 20—charges on complexes omitted)[103]. These differences even in schemes involving related ligands must be considered in establishing the dependence of the stability of the complexes on the basicity of the ligand. Here we can examine a few cases of interaction and the corresponding types of correlation.

1. One complexing metal ion reacts with different related ligands by a single scheme of complex formation. In this case lg β can be plotted against lg K_{eq} and against pK_{OH} (Figs. 2 and 3). Departures from these relations often indicate incorrect determination of K_{eq} or pK_{OH}.

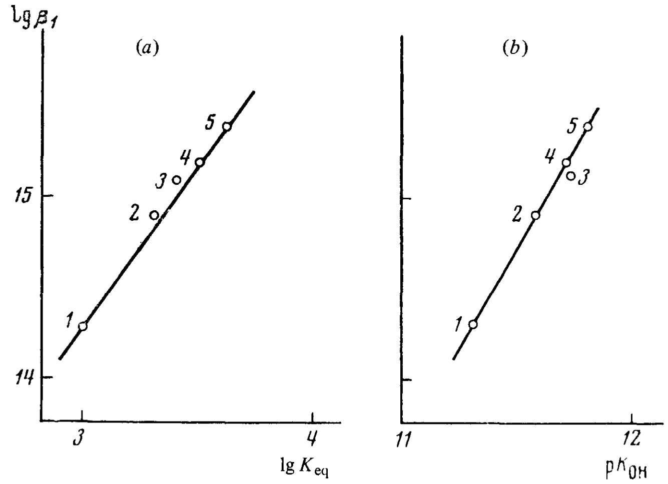


Figure 3. Effects of (*a*) complex-formation equilibrium constant and (*b*) basicity of ligand on stability of copper compounds of: *1*) 5-Cl-PAAC; *2*) 5-Br-PAAC; *3*) 5-Cl-PAAP; *4*) 1-PAN; *5*) 5-Cl-PAAP.[24]

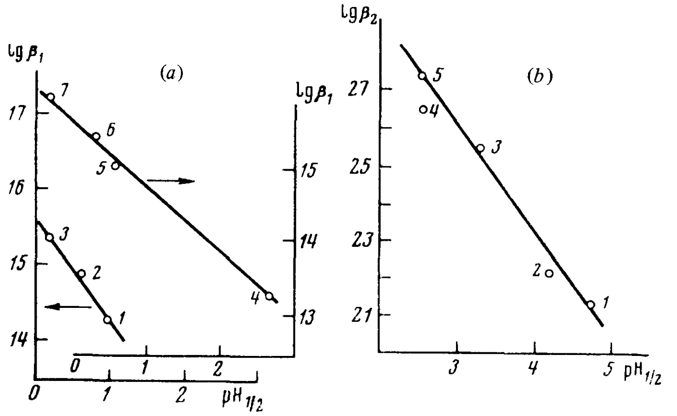


Figure 4. Effects of half-reaction pH on stability of: (*a*) copper compounds (1 : 1 complexes)[24] of: *1*) 5-Cl-PAAC; *2*) 5-Br-PAAC; *3*) 3,5-di-Br-PAAC; *4*) PAAP; *5*) 5-Cl-PAAP; *6*) 5-Br-PAAP; *7*) 3,5-di-Br-PAAP; (*b*) cobalt compounds (1 : 2 complexes)[9] of: *1*) PAR; *2*) 5-Br-PAR; *3*) 3,5-di-Br-PAR; *4*) tetrabromo-PAR; *5*) 2,6-dibromo-4-pyridylazoresorcinol.

A more universal relation is the dependence of lg β on pH$\frac{1}{2}$:

$$-n\,\mathrm{pH}_{1/2} = \lg K_p + n \lg C_R;$$

$$-n\,\mathrm{pH}_{1/2} = \lg \beta - n\,\mathrm{p}K_{OH} + n \lg C_R\ .$$

These results are plotted in Fig. 4 (for Cu : R = 1 : 1 and Co : R = 1 : 2) and were obtained on the assumption that the reagent concentration was 10^{-4}M. We can use these relations to estimate β from the experimental value of pH$\frac{1}{2}$ (by plotting the pH dependence of the optical density).

2. Several complexing metal ions react with a single ligand according to the same scheme. Here it is advisable to plot lg β against pH$\frac{1}{2}$ as in Figs. 4 and 5. For example, PAR is able to interact with metal ions according to several schemes, to form protonated and normal complexes (MRH and MR). For each scheme pH$\frac{1}{2}$ is calculated by means of the appropriate equation:

$$M + H_2R \rightleftarrows MRH + H^+,$$

$$-\mathrm{pH}_{1/2} = \lg \beta - \mathrm{p}K_{OH} + n \lg C_R;$$

$$M + H_2R \rightleftarrows MR + 2H^+ \text{ or } MRH \rightleftarrows MR + H^+,$$

$$-\mathrm{pH}_{1/2} = \lg \beta - \mathrm{p}K_{OH} - \mathrm{p}K_{p\text{-}OH} + n \lg C_R$$

where $\mathrm{p}K_{p\text{-}OH}$ is the logarithm of the reciprocal of the dissociation constant of the hydroxy-group *para* to the azo-group.

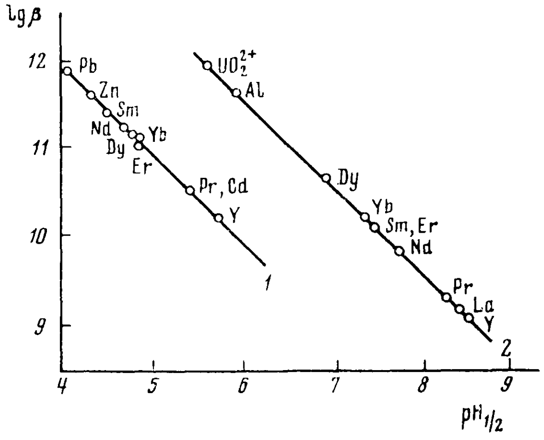


Figure 5. Stability sequences of PAR complexes: *1*) protonated (MRH); *2*) normal (MR). Constants for the rare-earth metal complexes taken from Ref. 80; that for uranium from Ref. 76; and those for lead, zinc, and cadmium from Ref. 17.

These relations enable us (*a*) to compare the stability of protonated and normal complexes of the same complexing agent, (*b*) to find lg β from the experimental value of pH$\frac{1}{2}$, (*c*) to construct a stability sequence of complexes of different complexing metals with the same ligand, and (*d*) to confirm a suggested scheme of complex formation by means of the values found for pH$\frac{1}{2}$ and lg β.

3. One complexing metal ion reacts with related ligands according to different schemes. No correlation of the above types is possible here: only the dependence of lg β on lg K_{eq} is applicable (Fig. 6). Exceptions are the normal complex with PAR of type MR formed at pH 3.9–4.5 and the complex with 5-Br-PAAP formed at pH 0.1–1.2 (protonated complex of type MRH). It is easy to explain these exceptions: investigation of complex formation between platinum(II) and PAR established[79] the effect of the acetate ion on the conditions of complex formation and on the properties of the complex, in particular the molar extinction coefficient ($10^{-4}\epsilon$ = 6.0). This suggests the formation of the mixed-ligand three-component compound platinum–acetate–PAR. All azo-derivatives of pyridine other than 5-Br-PAAP (at pH 0.1–1.2) react with platinum in weakly acid medium; the acidity ranges roughly coincide, which may indicate indirectly that the ionic state of the platinum is the same. The complex formed with 5-Br-PAAP in strongly acid medium probably contains platinum in a different ionic state from that occurring on interaction with other azo-derivatives of pyridine. Therefore the properties of the resulting complex differ markedly from those of complexes formed in weakly acid medium.

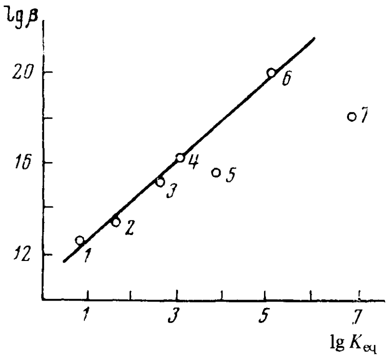


Figure 6. Effect of complex-formation equilibrium constants on stability of compounds of platinum(II) with pyridylazo-compounds[103]: *1*) 2-PAN; *2*) 5-Br-PAAP (ph < 2.0); *3*) PAAP; *4*) PAAC; *5*) PAR (ph < 4.5); *6*) PAR-(pH < 1.6); *7*) 5-Br-PAAP (pH ≃ 0).

Hence the scheme of complex formation can be confirmed by plotting lg β against lg K_{eq}.

4. Complexing metal ions adjacent in the Periodic System react with related ligands. If complex formation is described by a single scheme, correlations are present between the stability of complexes of two complexing metal ions as well as between the stabilities of complexes of two neighbouring metals in a series, and the basicity of the ligand (Figs. 7 and 8). Departure from the correlation usually indicates an incorrect value of the dissociation constant of the reagent for the actual conditions: it is necessary to compare constants determined by the same method.

Very large differences exist between the values given by different authors for the stability constants of the same complex, e.g. lg β = 9.8,[107] 17.93,[12] and 24.17[108] for compounds of PAR with thallium(III), and 10.0[107] and 14.5[6] for the gallium compounds. These differences are partly due to incorrect determination of the ratio of the components in the complex, the choice of scheme for complex formation, and the use of thermodynamic instead of conventional dissociation constants of the reagents, without taking into account the nature of the solvent and the dielectric constant of the medium.

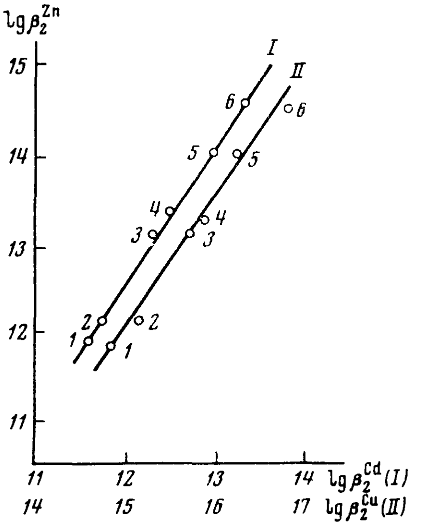


Figure 7. Relative stability constants (determined potentiometrically in 50% dioxan) of zinc, copper, and cadmium complexes[106] of compounds having the same type of ligands: *1*) 4-methyl-2-thiazol-2′-ylazophenol; *2*) 4-methoxy-2-thiazol-2′-ylazophenol; *3*) 2,4-dimethyl-6-thiazol-2′-ylazophenol; *4*) 4-methyl-2-(4,5,6,7-tetrahydrobenzothiazol-2-ylazo)phenol; *5*) 4-methoxy-2-4′-methylthiazol-2′-ylazophenol; *6*) 4-methoxy-2-(4,5,6,7-tetrahydrobenzothiazol-2-ylazo)phenol.

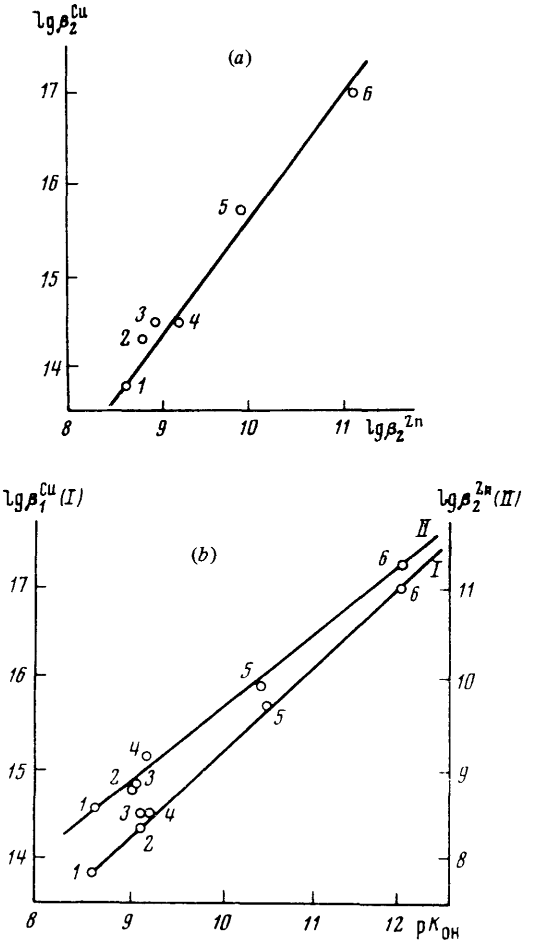


Figure 8. (*a*) Correlation of stability constants and (*b*) effect of basicity of ligands on stability of copper and zinc compounds[20] of: *1*) 1-PAN; *2*) 1-PAN-5-SO_3H; *3*) 1-PAN-7-SO_3H; *4*) 1-PAN-6-SO_3H; *5*) 1-PAN-8-SO_3H; *6*) 2-PAN.

Table 21. Methods of enhancing selectivity of reactions of heterocyclic azo-compounds with metal ions.

Method	Metals
Determination in acid medium	Cu[109], In[110], V[111], Sb[112,113], Pd[114]
Difference in rates of formation	Co, Cr[44,115,116], Pd, Rh[117], Pt[118]
Use of masking	Cu[64], Zn, Cd[119], Ga[120], In[110], Gd[121] lanthanide [122] U[123,124]
Coprecipitation of test elements	Co[9,125]
Electrodeposition of interfering elements	Sm[126], Ti, Nb[127], V[128]
Extraction of test ion	Cu[129], Zn[62], Ga[130], In[110], Nb[131]
Extraction of interfering elements	Zn[132], Nb[133], U[124], Mn[134, 135], Ni[136]
Re-extraction of test or interfering elements	Zr[137], Sn[138], V[139], Nb[140], Co, Ni[141]
Chromatographic separation	Mn[142], Co[143, 144], Ni[145]
Difference in absorption spectra	Fe[146], Ru, Os[147], Rh, Ir[148]

IV. SELECTIVITY OF HETEROCYCLIC AZO-COMPOUNDS

Heterocyclic azo-compounds are very widely used for the photometric and the extraction–photometric determination of ions of almost all metals, other than alkali and alkaline-earth metals, in naturally occurring and artificially produced materials. This is promoted by the high sensitivity of the reagents and the selectivity of their reaction with a series of ions. Several methods are available for enhancing the selectivity of reactions with organic ligands, some of which have been achieved with heterocyclic azo-compounds (Table 21).

The wide range of ions with which heterocyclic azo-compounds react and the possibility of the extraction of complexes combined with spectral analysis have permitted the determinations e.g. of copper, cobalt, cadmium, gallium, iron, indium, manganese, nickel, thallium, and vanadium in alkali-metal bromates and iodates (at concentrations of $7 \times (10^{-7}-10^{-5})$ mass %).[149] After being concentrated by extraction, many elements can probably be determined in a single aliquot by atomic absorption or polarographic methods. The specificity of heterocyclic azo-compounds can usefully be exploited in activation analysis.

V. PROSPECTS FOR STUDY AND USE IN ANALYTICAL CHEMISTRY

Extraction

This procedure may prove very useful for enhancing sensitivity, improving the selectivity of determination, and the study of complex formation. Although reagents are often employed for extraction-photometric determination, the extraction of complexes of heterocyclic azo-compounds has not been adequately characterised. Several studies have recently been published on rates of extraction[150–152] and on the effect of various solvents on the distribution of reagents between organic and aqueous phases[101,151,152]. The rules thus found can be used to raise the selectivity of reagents.

Mixed-ligand Compounds

The introduction of two ligands into the coordination sphere of a complex will often improve the sensitivity and the selectivity of reagents. Mixed-ligand (mixed) complexes of heterocyclic azo-compounds are beginning to be investigated intensively. Some examples of mixed complexes are listed in Table 22.

Table 22. Mixed-ligand complexes of heterocyclic azo-compounds.

Complexing metal	Heterocyclic azo-cpd..	Second ligand
Al^{III}	PAR	antipyrine[154]
Ga^{III}	PAR	antipyrine[155]
In^{III}	PAR	antipyrine[154]
	PAN	acetate, chloride[152]
Ti^{IV}	PAR	H_2O_2[156], SCN[157], acetate[158], catechol[159], salicylic and 5-sulphosalicylic acids[160]
	PAN	H_2O_2[161]
V^V	PAR	H_2O_2[111, 162], tetraphenylarsonium, tetraphenylphosphonium[163], diantipyrylmethane[164], quinine[165]
Nb^V	PAR	H_2O_2[166], oxalate, tartrate[50, 52]
	PAN	H_2O_2[161]
Ta^V	PAR, PAN	H_2O_2[161, 166]
Mo^{VI}	PAR,TAR	hydroxylamine[167, 168]
Fe^{II}	PAR	hydroxylamine[169]
Co^{III}	PAR	quaternary ammonium bases[169]

Preparation of New Reagents

Besides the above heterocylic amines, derivatives of pyrrole[170], imidazole[171], antipyrine[172], triazole[19], tetrazole[173,174], and thiadiazole[175] have been used as bases, and bisazo-compounds have been prepared[173,174,176–178]. However, azo-derivatives of pyridine have hitherto been the most promising. The synthesis has begun of compounds containing as coupling components reagents that are themselves widely used in analytical chemistry, e.g. azo-derivatives of rhodanine[179–184], catechol[92,97,185–187], and chromotropic acid. The reagents possess several advantages in comparison with these compounds: stepwise complex formation is absent, the stability of the complexes is increased, and maximum absorption by the complexes takes place at longer wavelengths. This method is evidently most useful in the synthesis of new reagents.

Research Methods

Extraction has begun to be used as well as the widely employed photometric and potentiometric methods. The characteristics of the complex compounds are obtained by computer methods according to suggested programmes[96,171,188–190]; the advantages of such methods have been demonstrated many times. The structures of complex compounds and reactive forms of reagents are established by quantum-chemical calculations[22,23,191,192], nuclear magnetic resonance[193], determination of magnetic and dipole moments of the complexes[194,195], and by study of the infrared spectra[50,52,193,196–199].

* * *

Heterocyclic azo-compounds are widely used as reagents for the photometric determination of elements and as complexometric indicators. The most sensitive are azo-derivatives of pyridine and 2-aminoquinoline, which form stable compounds with metal ions. A hydroxy-, amino-, or dialkylamino-group can usefully be introduced into the coupling component *para* to the azo-group to improve the properties of the reagents. A halogen—chloro or bromo—must be substituted *para* to the azo-group in the pyridine base. Promising complexometric indicators are thiazolylazo-compounds, which form intensely coloured and moderately stable compounds with metal ions. The solubility of these reagents can be increased by sulphonating the coupling component and the base. Reagents containing heterocyclic nitrogen in the coupling component—quinolinol, 2,6-dihydroxypyridine, etc. — should be valuable for the determination of readily hydrolysed ions of multivalent metals. Promising uses of extraction are the investigation of complex formation and the concentration of groups with the aim of subsequent polarographic, spectral, or atomic-absorption determination.

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Silicon-containing Derivatives of Carbamic Acid—Silylurethanes

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Methods of synthesis, properties, and likely applications of silicon-containing derivatives of carbamic acid—silylurethanes—are discussed for the first time. Together with monomeric compounds, oligomeric and polymeric products as well as various compositions based on them, containing silicon and urethane groups, are considered. The review includes studies which have been published up to the middle of 1975.

The bibliography consists of 527 references.

CONTENTS

I. INTRODUCTION

The chemistry of silyl derivatives of carbonic acid, i.e. of organosilicon carbonates, chloroformates, isocyanates, ureas, urethanes, carbodiimides, etc. began to develop only in the last decade in connection with the suggested applications of such compounds.

The present review completes a series of surveys of new organosilicon materials[1-10] and is closely related to the previous surveys devoted to silyl derivatives of carbonic acid-organosilicon isocyanates[11] and ureas[12].

In terms of structural features, silyl derivatives of carbamic acid can be divided into three main types. In the first type of silylurethanes, the so called *O*-silylurethanes, we include compounds with the structural element $\equiv Si-O-C(O)-N=$. The second type incorporates *N*-silylurethanes, characterised by the fragment $\equiv Si-\overset{|}{N}-C(O)-O-$. Finally, we have silicon-containing urethanes with a carbon-based functional group in which the carbamic acid group is linked to the silicon atom via a hydrocarbon bridge. In the last case it is useful to introduce a subdivision of the silylurethanes into independent groups containing the bond sequences $\equiv Si-R-O-C(O)-N=$ and $\equiv Si-R-\overset{|}{N}-C(O)-$. Very many examples of each of these groups are now known.

II. COMPOUNDS WITH THE URETHANE GROUP AT THE SILICON ATOM

There are 12 theoretically possible structures of this type:

$R_3SiOC(O)NH_2$ (I); $R_3SiOC(O)NHSiR_3$ (II); $R_3SiOC(O)N(SiR_3)_2$ (III);
$R_3SiOC(O)NHR$ (IV); $R_3SiOC(O)N(R)SiR_3$ (V); $R_3SiOC(O)NR_2$ (VI)
$R_3SiNHC(O)OH$ (VII) $R_3SiN(R)C(O)OH$ (VIII) $(R_3Si)_2NC(O)OH$ (IX)
$R_3SiNHC(O)OR$ (X) $R_3SiN(R)C(O)OR$ (XI) $(R_2Si)_2NC(O)OR$ (XII)

but only nine are actually known: (I)-(VI) and (X)-(XII). Incidentally, the carbamic acids (VII)-(IX) can hardly exist in a free state, since, owing to the ease of the silyl-proton exchange, they must be immediately converted into the *O*-silyl derivatives (I)-(VII).

1. METHOD OF SYNTHESIS

N-Silylurethanes

N-Monosilyl-substituted carbamic acid esters were obtained for the first time in 1959[13,14] by the silylation reaction

$$Q{-}NHSiMe_3 + ROC(O)NH_2 \rightarrow ROC(O)NHSiMe_3 + Q{-}NH_2;$$
$$Q{=}Alk,\ Ar,\ AlkC(O),\ ArC(O).$$

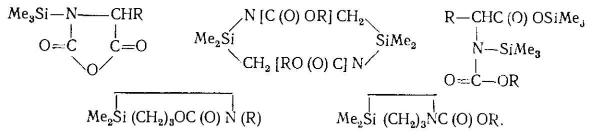
The silylation of the urethane $EtOC(O)NH_2$ by chlorotriorganylsilanes in the absence of acceptors for the HCl released apparently does not occur and the authors claim concerning the possibility of the conversion of the resulting *N*-silylurethanes with boiling water or alkali into the water-soluble acids $R_3SiNHC(O)OH$ is clearly erroneous, since no account is taken of the susceptibility of the N–Si bond to hydrolysis and the instability of free carbamic acid[15].

The interaction of urethane with $SiCl_4$ leads to the formation of the complex $SiCl_4.6CO(NH_2)_2$ (Wannagat et al.[16]), tentatively via the following mechanism:

$$2\,EtOC(O)NH_2 \rightarrow NH_2C(O)NH_2 + CO(OEt)_2;$$
$$SiCl_4 + 6CO(NH_2)_2 \rightarrow SiCl_4 \cdot 6\,CO(NH_2)_2;$$
$$SiCl_4 + 4CO(OEt)_2 \rightarrow Si(OEt)_4 + 4\,EtCl + CO_2.$$

Subsequently, when Me_3SiCl or $Me_3SiCl/HN(SiMe_3)_2$ were used as the silylating systems in the presence of organic bases and the reaction was carried out in aprotic organic solvents, *N*-silylurethanes became readily available. Numerous *N*-silyl derivatives of both linear and cyclic urethanes were obtained by this procedure[17-34]:

$R_3Si(CH_2)_nN(SiMe_3)C(O)OR$ $(R_3Si)_2NC(O)OR;$



The expected urethane could not be isolated after the reaction between Ph_3SiCl and $NaNHC(O)OEt$, since its β-decomposition resulted in the formation of Ph_3SiNCO in 48% yield[35]:

$$Ph_3SiNHC(O)OEt \rightarrow Ph_3SiNCO + EtOH.$$

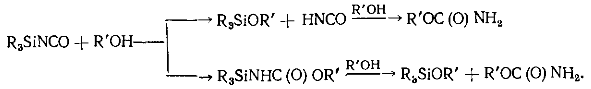
N-Silylurethanes have been synthesised in high yields by the reactions of alkylbis(trimethylsilyl)amines and alkyl chloroformates[27]:

$$RN(SiMe_3)_2 + ROC(O)Cl \rightarrow RN(SiMe_3)C(O)OR.$$

The reaction of chloroformates with hexamethyldisilazane (HMDS) and $R'NHSiR_3$, which proceeds preferentially via the Si–N bond rather than N–H, is of limited importance[36,37]:

$$(Me_3Si)_2NH + ROC(O)Cl \rightarrow Me_3SiNHC(O)OR + Me_3SiCl$$
$$R'NHSiMe_3 + ROC(O)Cl \rightarrow R'NHC(O)OR + Me_3SiCl.$$

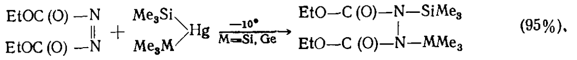
The attempt to synthesise *N*-silylurethanes via the reactions of isocyanatosilanes with alcohols[11,26,35–44] and silanols[45–51] was unsuccessful owing to the ease of the alcoholysis of the N–Si bond and the inertness of silanols. The reaction with alcohols can be represented by the following mechanisms of which the second is to be preferred:



$$R_3SiNCO + R'OH \rightarrow R_3SiOR' + HNCO \xrightarrow{R'OH} R'OC(O)NH_2$$
$$R_3SiNCO + R'OH \rightarrow R_3SiNHC(O)OR' \xrightarrow{R'OH} R_3SiOR' + R'OC(O)NH_2.$$

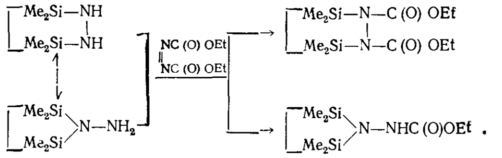
An increase in the size and branching of the groups in both the silane and the alcohol leads to a fall of the rate of alcoholysis[35,39] and Ph_3SiNCO does not change at all in boiling benzene in the presence of alcohol[35].

N-silyl-substituted esters of carbazic acids, which have been obtained from mercury-containing reagents[52–54], constitute a group of *N*-silylurethanes having the same structure:



$$EtOC(O){-}N{=}N{-}C(O)OEt + (Me_3Si)(Me_3M)Hg \xrightarrow[M=Si,\,Ge]{-10^\circ} EtO{-}C(O){-}N(SiMe_3){-}N(MMe_3){-}C(O){-}OEt \quad (95\%).$$

They have also been obtained on the basis of equilibrium mixtures of tautomeric froms of disilyl-substituted hydrazines[55], for example:



Silylurethanes of the type $ROC(O)N(SiR'_3)_2$ are not formed by the above reactions. They have been synthesised by the reaction of $NaN(SiMe_3)_2$ with alkyl chloroformates[56] and, by analogy with bis(trimethylsilyl)amides of carboxylic acid, the imide structure (XIII) has been attributed to them:

$$ROC(O)Cl \xrightarrow[-NaCl]{NaN(SiMe_3)_2} ROC(O)N(SiMe_3)_2 \longleftrightarrow \underset{(XIII)}{ROC(=NSiMe_3)OSiMe_3}.$$

When these compounds were hydrolysed with an equimolar amount of water, *N*-monosilylurethanes were obtained:

$$2ROC(=NSiMe_3)OSiMe_3 \xrightarrow{H_2O} 2ROC(O)NHSiMe_3 + Me_3SiOSiMe_3.$$

O-Silylurethanes

The principal method for the synthesis of these compounds is carboxylation of aminosilanes[57–75]:

$$(R'R''N)_nSiR'''_{4-n} \xrightarrow[n=1\div4]{n\,CO_2} [R'R''NC(O)O{-}]_nSiR'''_{4-n};$$
$$R', R''=H, Alk, AlkO, Ar;\ R'''=Alk, Ar,$$

which proceeds via an ionic-chain mechanism[62,63,70–73] and as a rule leads to the formation of the desired product in quantitative yield.

Compounds with a reduced basicity constitute exceptions to the general series of aminosilanes[60,61,69,73,76,77]: $MeN(SiH_3)_2$, $HN(SiMe_3)_2$†, $AlkN(SiMe_3)_2$, $AlkN(SiMe_2H)_2$, $PhNHSiMe_3$, $MeC(O)NHSiMe_3$, and $MeC(O)N(SiMe_3)_2$. Incidentally under severe conditions the following reaction takes place[69]:

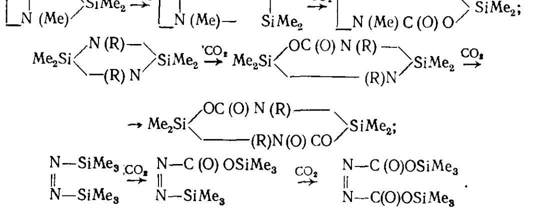
$$RN(SiMe_3)_2 \xrightarrow[500^\circ]{CO_2} [R{-}N(SiMe_3)C(O)OSiMe_3] \rightarrow RNCO + (Me_3Si)_2O.$$

However, when a mixture of a weakly basic amine and the silylating agent is carboxylated, it is nevertheless possible to obtain the corresponding *O*-silylurethanes, since in this case the species silylated is the intermediate carbamic acid in which the hydrogen atom is dissociated to an incomparably greater extent[73]. For example:

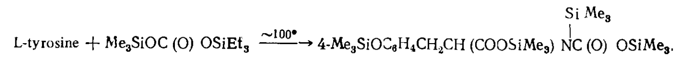
$$PhNH_2 + CO_2 \rightarrow PhNHC(O)OH \xrightarrow{H-N(SiMe_3)_2} PhNHC(O)OSiMe_3.$$

Urethanes are then formed rapidly and in high yields.

In many instances carboxylation of compounds with several Si–N bonds proceeds in steps and leads to adducts with both one and two CO_2 molecules[66,74,78–80]:



Aminoacids containing silicon-substituted carbamic acid groups are obtained with the aid of a wide variety of silylating agents[20,81–87]: Me_3SiCl/NEt_3, $HN(SiMe_3)_2$, organosilylcarbonates, etc. For example:



$$\text{L-tyrosine} + Me_3SiOC(O)OSiEt_3 \xrightarrow{\sim100^\circ} 4\text{-}Me_3SiOC_6H_4CH_2CH(COOSiMe_3)N(SiMe_3)C(O)OSiMe_3.$$

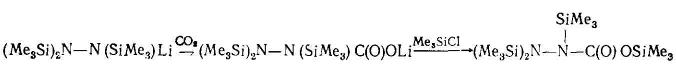
O-Silylurethanes can also be obtained by the silylation of carbamic acids or their salts by the usual procedures[34,64,66,85,87]:

$$R_2NC(O)OH + Me_3SiCl + R_3N \rightarrow R_2NC(O)OSiMe_3 + R_3N \cdot HCl;$$
$$H_2NC(O)ONH_4 + Me_3SiCl \rightarrow H_2NC(O)OSiMe_3 + Me_3SiNHC(O)OSiMe_3.$$

We believe that the reaction of silylated alkali metal amides with CO_2 followed by the reaction of the intermediate sodium salts, for example of *NO*-disilylated carbamic acids, with chlorosilanes[88–93] may become a convenient method for the synthesis of such compounds:

$$(Me_3Si)_2NNa \xrightarrow{CO_2} (Me_3Si)_2NC(O)ONa \xrightarrow{Me_3SiCl} (Me_3Si)_2NC(O)OSiMe_3.$$

This view is supported by the successful reaction with the lithium salt of carbazic acid[66]:



$$(Me_3Si)_2N{-}N(SiMe_3)Li \xrightarrow{CO_2} (Me_3Si)_2N{-}N(SiMe_3)C(O)OLi \xrightarrow{Me_3SiCl} (Me_3Si)_2N{-}N(SiMe_3){-}C(O)OSiMe_3$$

In order to obtain *O*silylurethanes, the interaction of silanols with organic and organosilicon isocyanates has been investigated and it has been shown that Ph_3SiOH and $Ph_2Si(OH)_2$ do not interact with Me_3SiNCO owing to steric hindrance and the reduced nucleophilic properties of the nitrogen atom in isocyanatosilane[49,94]. On the other hand, it has been established that $Me_3Si(NCO)_2$ acts on $Ph_2Si(OH)_2$ as a dehydrating agent. The reaction of monofunctional

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† It has been stated[64] that $Me_3SiNHC(O)OSiMe_3$ is formed in a negligible yield on carboxylation of HMDS in tetrahydrofuran.

organic isocyanates with silanediols and oligosiloxanes containing terminal hydroxyls proceeds similarly[49,94-98].

Even if organosilicon polyurethanes $[-OSiR_2OC(O)NHR'NHC(O)-]_n$ (OSPU) are formed in the polycondensation of dialkylsilanediols and polyalkylsiloxanediols with hexamethylene and tolylene diisocyanates, oligourethanes with terminal isocyanato-groups, and other similar prepolymers, their yields are insignificant[51,99-106] and the reaction results mainly in the evolution of CO_2 and water and the formation of organic polyureas and polysiloxanes‡ :

$$HOSiR_2OH + OCN-R'-NCO \rightarrow [-NHC(O)NHR'-]_n + -[-SiR_2O]_n + CO_2.$$

It has been suggested that the reaction of $\equiv SiOH$ groups with PhNCO be used for the quantitative determination of OH groups in polyorganylsiloxanes[105]. Subsequently it proved possible to find conditions in which *O*-silylurethanes can be obtained from aromatic diisocyanates and trialkylsilanols[107-109]:

$$R_3SiOH + Q(NCO)_2 \rightarrow Q[NHC(O)OSiR_3]_2.$$

In this connection one should note that, since the reaction of silanols with isocyanates was carried out in most cases at high temperatures or in the presence of aluminium chloride[46,47,51,97,98,104-106,111-128], this may have been the reason why the reactions did not yield the corresponding polyurethanes, their decomposition products being formed instead: CO_2, H_2O, and mixtures of organic and organosilicon high-molecular-weight compounds. However, since such materials possess properties of practical value, some of them will be considered in Section V.

In conclusion we may note that the study of the sorption of BuNCO[129,130] and PhNCO[131] vapours by aerosil showed that two processes occur: physical sorption and chemisorption. The former is due to the hydrogen bonds formed between the isocyanate and the free silanol groups of the adsorbent, which probably creates conditions for the occurrence of a chemical reaction between the isocyanates and the hydroxy-groups with formation of urethane groups.

2. PHYSICAL PROPERTIES OF *N*- AND *O*-SILYL URETHANES

O-Silylurethanes

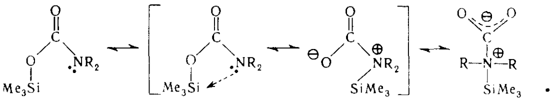
Urethanes of this type are high-boiling liquids or white crystalline, sometimes wax-like, substances which are more readily soluble in aprotic organic solvents[26,32,52,63-66,69,76,77,107-109,114]. Thixotropic properties are characteristic of organosilyltriscarbamates[58].

The combination of infrared, ultraviolet, and ^1H, ^{15}N, and ^{29}Si NMR data has shown that the N–Me groups in $Me_2NC(O)OSiH_3$ are equivalent, which is caused either by the rapid migration of the silyl group between the neighbouring oxygen atoms or by the ease of rotation about the C–N bond in consequence of its weak double bond character[60-62,76].

However, it was subsequently shown that trimethylsilyl esters of carbamic, thiocarbamic, and dithiocarbamic acids are characterised by different amounts of double bond character of the C–N linkage. For example, the study of the effect of the hindered internal rotation about the C–N bond in compounds described by the general formula $Me_3Si-Y-C(=X)-NR_2$, where X, Y = O, O, or S, S and R = Me or Et showed that it depends on temperature[132,133]. The experimental effective lifetimes of the rotational isomers made it possible to determine the activation energy and the free energy for the intramolecular rotation process and to compare them with the types of substituents surrounding the carbamic acid groups.

The infrared spectra of *O*-silylurethanes with an exocyclic carbamic acid group are characterised by absorption bands at 1020–1080, 1665–1690, and 3340–3350 cm^{-1}, which are due to the stretching vibrations of the Si–O–C, C=O, and N–H linkages[26,56,60-62,64,73,76,77]. One must note that the intensity of the Si–OC absorption band is very low.

We believe that the moderate solubility of *O*-silylurethanes, their high boiling and melting points despite their comparatively low molecular weights, the degenerate nature of the Si–O–C absorption band, and the specific features of the ^1H NMR spectra discussed above can be accounted for by their existence in equilibrium with the ylid form (XIVd):



(XIVa) (XIVb) (XIVc) (XIVd)

Under electron impact conditions, the molecules of the *O*-silylurethanes $Me_3SiOC(O)NH_2$ and $Me_3SiOC(O)NHSiMe_3$ each lose an electron and their mass spectra are characterised by molecular ion peaks[64].

N-Silylurethanes

Compounds of the type $R'N(SiR''_3)C(O)OR'''$, where R′ = Me, Bz§, α-naphthyl, or $N(SiMe_3)_2$, R″ = Me or Et, and R‴ = Me, Et, or Ph are mobile liquids or low-melting crystalline solids, readily soluble in the majority of the usual aprotic organic solvents[23,26,36,66], with the exception of n-hexane, petroleum ether, and carbon tetrachloride[26,36]. Their infrared spectra agree well with the amide structure[26,36]. The molar refractions of *N*-silylurethanes correspond rigorously to the theoretical values[26].

NO-Disilylurethanes

Disilyl-substituted urethanes and carboxylic acid amides are very close analogues. The non-equivalence of the Me_3Si protons in the ^1H NMR spectra at low temperatures is characteristic of the latter compounds, disappearing when the temperature is raised to a particular value in each specific case. On this basis and also on the basis of infrared spectroscopic data and certain chemical reactions, the structure of *N*-trimethylsilyl-*O*-trimethylsilyliminoesters (XVb) with rapid intramolecular two-centre exchange of the partially ionically bound Me_3Si groups between the N and O atoms in (XVb) at elevated temperatures, rather than the structure of *NN*-bis(trimethylsilyl)acylamides (XVa), was attributed to these compounds[56,134-138].

$$\underset{(XVa)}{R-C(O)N(SiMe_3)_2} \rightleftarrows \underset{(XVb)}{R-C(=NSiMe_3)OSiMe_3}\ .$$

Depending on the nature of the substituents linked to the silylamide group, the rate of migration of the Me_3Si group varies, which many investigators[134,138] believe to be a manifestation of the different degrees of hindrance of the

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‡ Aniline, $Ph_3SiOSiPh_3$, symmetrical diphenylurea, and unidentified silicon-containing polyurethanes have been isolated after the reaction of Ph_3SiOOH and PhNCO.[110]

§ Bz = benzyl.

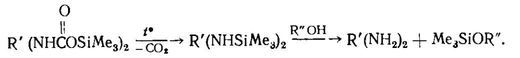
intramolecular rotation about the C–N bond. On passing from the disilyl amides $RC(=NSiMe_3)OSiMe_3$ to the disilylurethanes $ROC(=NSiMe_3)OSiMe_3$, the rate of exchange of the silyl groups increases and remains high even at low temperatures[56], while the $SiMe_3$ group is revealed by a singlet in the ^1H NMR spectrum.

3. CHEMICAL PROPERTIES OF *N*- AND *O*-SILYLURETHANES

O-Silylurethanes

O-Silylurethanes monoalkyl(aryl)-substituted at the nitrogen atom are extremely sensitive to hydrolysis, which proceeds via the formation of unstable carbamic acids, decomposing into CO_2 and amines[57–59,65,70,72,106–109].

The reactions with alcohols lead to the formation of CO_2, amines, and orthosilicate esters[108]. The authors suggest that hydrolysis (initially by traces of water in the alcohol), leading to the formation of trialkylsilanols, amines, and CO_2, takes place in the first stage. The trialkylsilanols then react with alcohols to form the corresponding orthosilicate esters and water[108]. However, we believe that a more convincing hypothesis is, for example, that the first stage involves the familiar decarboxylation reaction of urethanes[63,65,69,77] with subsequent alcoholysis of the resulting aminosilane:



$$R'(NH\overset{\overset{O}{\|}}{C}OSiMe_3)_2 \xrightarrow[-CO_2]{t^\circ} R'(NHSiMe_3)_2 \xrightarrow{R''OH} R'(NH_2)_2 + Me_3SiOR''.$$

This conclusion is also confirmed by the finding that urethanes of the type $R_2NC(O)OSiR'_3$, which are no less susceptible to hydrolysis than those discussed above but which do not undergo decarboxylation, fail altogether to react with alcohols.

When the urethanes $RNHC(O)OSiMe_3$ are heated to 100–130°C, they undergo complete and irreversible decomposition to the corresponding disiloxanes and symmetrical ureas[69,77]. Pyrolysis in the presence of reactive chlorosilanes, for example $SiCl_4$ or $RSiCl_3$, alters the nature of the side reactions and the final products are an organic isocyanate, HCl, Me_3SiCl, and chlorosiloxanes[69,77]:

$$RNHC(O)OSiMe_3 + SiCl_4 \rightarrow RNHC(O)OSiCl_3 + Me_3SiCl;$$

$$RNHC(O)OSiCl_3 \rightarrow RNCO + [HOSiCl_3] \text{ etc.}$$

It has been noted that the use of other chlorosilanes (Me_2SiCl_2, Ph_2SiCl_2) is less effective, since decarboxylation of *O*-silylurethanes is observed in this case.

The formation of isocyanates proceeds satisfactorily in the presence of $SOCl_2$ and PCl_5.

When urethanes of the type $RR'NC(O)OSiMe_3$ were treated with $COCl_2$, $SOCl_2$, PBr_3,[66,139] and PCl_5,[140] the corresponding carbamoyl chlorides were obtained. It is noteworthy that, when the molecule contains both *N*- and *C*-siloxycarbonyl groups, the carbamic acid group reacts first[66,83,139], for example:

$$Me_3SiOC(O)N(R)(CHR')_nC(O)OSiMe_3 \xrightarrow[-Me_3SiX]{+YX_2}$$

$$\rightarrow XC(O)N(R)(CHR')_nC(O)OSiMe_3;$$

$$R{=}H,\ Alk,\ SiMe_3;\ R'{=}H,\ Alk;\ X{=}Cl,\ Br;$$

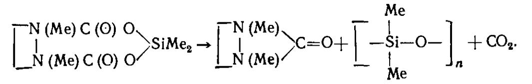
$$Y{=}{>}SO,\ {>}CO,\ {>}PBr,\ {>}PCl_3;\ n{=}1,2.$$

Apart from the thermally initiated decarboxylation noted above[63,65,69], the possibility of the disproportionation reaction has been demonstrated[64] for $Me_3SiOC(O)NH_2$:

$$2\,Me_3SiOC(O)NH_2 \rightarrow Me_3SiOC(O)NHSiMe_3 + [H_2NC(O)OH];$$

$$[H_2NC(O)OH] \rightarrow NH_3 + CO_2.$$

The cyclic *O*-silylurethane (XVI) is formed most readily when 1,1,2,5-tetramethyl-1-silaimidazolidine is treated with CO_2, being subsequently converted into polydimethylsiloxane, CO_2, and the corresponding imidazolidinone, probably via the following mechanism:



(XVI)

N-Silylurethanes

Urethanes of the type $MeN(SiMe_3)C(O)OR$, where R = Me or Et, are known not to interact with keten, but they do react with triethylsilylacetyl chloride to form $Et_3SiCH_2C(O)\cdot N(Me)C(O)OR$ in moderate yields[141].

N-Monosilyl-substituted amidals, which are at the same *N*-silylurethanes, undergo a symmetrisation reaction on heating and are then converted via β-decomposition into methylene diisocyanate[27,142]:

$$2\,CH_2[NHC(O)OR]N(SiMe_3)C(O)OR \rightarrow CH_2[N(SiMe_3)C(O)OR]_2 \rightarrow OCN{-}CH_2{-}NCO.$$

Other reactions of *N*-silylurethanes, for example *trans*-silylation and β-decomposition, are discussed in Section III (Subsections 3 and 4 respectively).

III. ORGANOSILICON URETHANES CONTAINING CARBON-BASED FUNCTIONAL GROUPS

1. METHODS OF SYNTHESIS

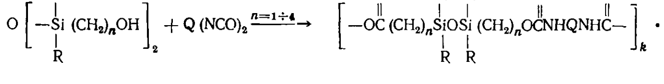
O-Silylorganyl Derivatives of Carbamic Acid

The reactions of organosilicon alcohols, glycols, and phenols (in which the functional groups are linked to carbon atoms) with isocyanates constitute a general method for the synthesis of *O*-silylorganylurethanes. For example, monohydric organosilicon alcohols[143–152] and phenols[153] readily give rise to the corresponding urethanes on reaction with both aliphatic and aromatic isocyanates:

$$R_3Si{-}Q{-}OH + R'NCO \rightarrow R_3Si{-}Q{-}OC(O)NHR' \quad (Q = \text{alkylene or arylene}).$$

It has been established that the reactivity of the hydroxy-group in homologous series of the alcohols $R_3Si(CH_2)_nOH$ and glycols $O[SiR_2(CH_2)_nOH]_2$ with $n = 1–3$ decreases as it becomes more remote from the silicon atom in the reactions with phenyl, octadecyl, and α-naphthyl isocyanates[148,149,151,152,154]. This is probably due to the rapid decay of the $+I$ effect of the electron-donating silyl group and the effect of the $(\sigma{-}p)$ conjugation of the Si–C bonds with the lone electron pair of the oxygen atom.

Polymeric urethanes have been obtained from the above glycols and organic diisocyanates, for example, hexamethylene (HMDI), *p*-phenylene (*p*-PDI), 1,5-naphthylene (1.5-NDI), tolylene (TDI), *pp*′-diphenylcyclohexyl, and *pp*′-diphenylmethylene diisocyanates[154–176]:



$$O\left[-\underset{R}{\overset{R}{Si}}(CH_2)_nOH\right]_2 + Q(NCO)_2 \xrightarrow{n=1\div 4} \left[-O\overset{O}{\overset{\|}{C}}(CH_2)_n\underset{R}{\overset{R}{Si}}O\underset{R}{\overset{R}{Si}}(CH_2)_nO\overset{O}{\overset{\|}{C}}NHQNH\overset{O}{\overset{\|}{C}}-\right]_k \cdot$$

Polyurethanes with a high silicon content (compounds (XVII) and XVIII)] are formed from oligosiloxanes containing hydroxyalkyl groups at the ends of the siloxane chain[158, 160,165,167,169,171,173,177-181] or in the side groups surrounding the chain[159,161-165,182]:

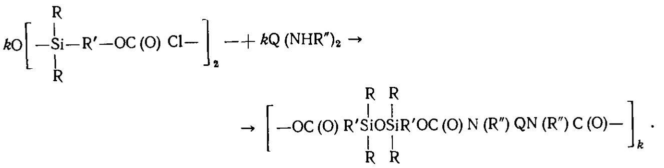
$$\underset{\text{(XVII)}}{HO(CH_2)_nSi(R_2)[OSiR_2-]_m-(CH_2)_nOH} \quad \underset{\text{(XVIII)}}{-[-OSi(R_2)(CH_2)_nOH-]_k-}.$$

Treatment of the products (XVII) and (XVIII) with monoisocyanates leads to oligosiloxanes modified by urethane groups[182]. Oligourethanes with terminal OH or OCN groups have been obtained by combining the glycols (XVII) with silicon-containing diisocyanates having carbon-based functional groups[175,183].

Apart from polyurethanes with an oxygen atom between silicon atoms, products with methylene, polysilamethylene, and ferrocenyl bridges or altogether without any bridges are also known[160,169,171,179].

More complex compositions are produced when the above glycols are initially converted by standard procedures into oligoesters and are then cross-linked by diisocyanates or the structures are modified by a polyisocyanate adduct containing biuret groups[157,168,174].

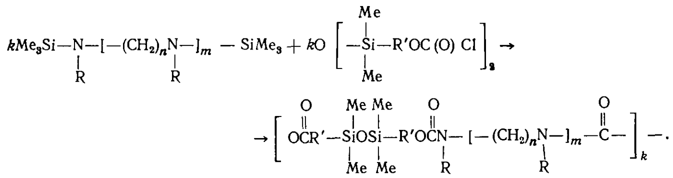
The synthesis of O-silylorganylurethanes by the aminolysis of organosilicon chloroformates[2,26,31,184-187] is also a general procedure. Condensation of bischloroformates of the disiloxane series with organic di- and poly-amines leads to the corresponding polyurethanes[2,151,188-191]:



$$kO\left[-\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}-R'-OC(O)Cl-\right]_2-+kQ(NHR'')_2 \rightarrow \rightarrow \left[-OC(O)R'\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}O\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}R'OC(O)N(R'')QN(R'')C(O)-\right]_k.$$

Instead if diamines, hydrazines, dihydrazines, piperazine, and polyamines of the general type $H(R)N[-(CH_2)_n.N(R)-]_mH$, where R = M, n = 2 or 3, and m = 1 or 2, have also been used.

When the above starting compounds are replaced by their $\alpha\omega$-bis(trimethylsilyl) derivatives, the polycondensation is significantly simplified, since Me_3SiCl formed in the reaction is inert and can be readily removed[2,190,192]:



$$kMe_3Si-\underset{\displaystyle R}{N}-[-(CH_2)_n\underset{\displaystyle R}{N}-]_m-SiMe_3+kO\left[-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-R'OC(O)Cl\right]_2 \rightarrow \rightarrow\left[O\overset{\displaystyle O}{\overset{\|}{C}}R'-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}O\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-R'O\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle R}{N}-[-(CH_2)_n\underset{\displaystyle R}{N}-]_m-\overset{\displaystyle O}{\overset{\|}{C}}-\right]_k-.$$

The reactions involving the aminolysis of organosilicon carbonates with carbon-based functional groups are of preparative value for the synthesis of O-silylorganylurethanes[193-198]:

$$RMe_nSi-[-(CH_2)_mOC(O)OPh]_{3-n} \xrightarrow{NH_3} RMe_nSi-[-(CH_2)_mOC(O)NH_2]_{3-n},$$

as well as the reactions of silicon-containing alcohols with alkali metal cyanates in CF_3COOH[26,198,199]:

$$\equiv Si(CH_2)_nOH+KOCN \xrightarrow[n=1\div3]{CF_3COOH} \equiv Si(CH_2)_nOC(O)NH_2.$$

The hydrosilylation of O-alkenylurethanes, whereby it is possible to obtain urethanes with different numbers of functional substituents at the silicon atom[26,31,200-202], constitutes an interesting addition to the above procedures, for example:

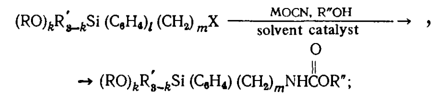
$$RR'NC(O)OCH_2CH{=}CH_2+HSiR''_nX_{3-n} \xrightarrow[n=1\div3]{X=Cl,\,OR} RR'NC(O)O(CH_2)_3SiR'_nX_{3-n}.$$

N-Silylorganylcarbamic Acid Derivatives

The reaction of organosilicon isocyanates containing carbon-based functional groups with alcohols¶ leads to urethanes with the silicon atom in the imide component of the molecule[26,178,183,203-211]:

$$R_3Si(CH_2)_nNCO+R'OH \xrightarrow{n\geqslant1} R_3Si(CH_2)_nNHC(O)OR'.$$

A modification of this method involves the interaction of halogenoalkylsilanes with alkali metal cyanates and the alcohol in molar aprotic solvents in the presence of $[(Alk)_4N]I$ as the catalyst[26,184,198,202,212,214], since organosilicon isocyanates are intermediates in this reaction:



$$(RO)_kR'_{3-k}Si(C_6H_4)_l(CH_2)_mX \xrightarrow[\text{solvent catalyst}]{MOCN,\ R''OH}, \rightarrow (RO)_kR'_{3-k}Si(C_6H_4)(CH_2)_mNH\overset{\displaystyle O}{\overset{\|}{C}}OR'';$$

R, R′=Alk, Ar; M=K, Na; X=Cl, Br; $k=1\div3$; $l=0, 1$; $m=1\div3$.

The reactivity of bromoalkylsilanes is higher than that of the chloro-derivatives and among the latter α-chloroalkylsilanes are the most reactive. On the other hand, the reactivity of the corresponding silyl isocyanates falls as the silyl and isocyanato-groups approach one another. Indeed, it has been shown in a number of investigations[26,178,183,203,205,207-210,213,215-217] that the reactivities of $(EtO)_3Si(CH_2)_3NCO$, $Et_3Si(CH_2)_3NCO$, and organic aliphatic isocyanates are comparable and approximately 20 times higher than that of Et_3SiCH_2NCO. The side products in the above reaction are organosilicon ureas and dimers (uretidinediones) and trimers (isocyanourates) of organosilicon isocyanates[26,212,213].

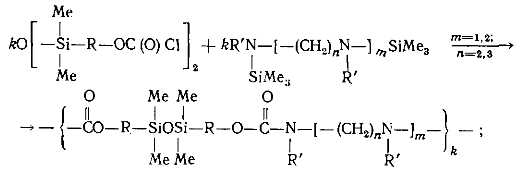
Polyurethanes with a silicon atom in the ester and amide components of the macromolecule simultaneously have been obtained by the condensation of silicon-containing diisocyanates and organosilicon glycols[178,183,208].

The interaction of alkyl(aryl)aminoalkylsilanes with organic chloroformates also leads to N-silylorganourethanes[201,218-220]:

$$\equiv Si(RNHR')_m \xrightarrow[m\geqslant1]{R''OC(O)Cl} \equiv Si[RN(R')C(O)OR'']_m,$$

but this method of synthesis holds out little promise, since half of the aminosilanes is consumed in binding HCl.

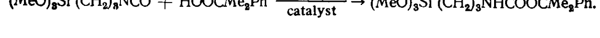
A modification of this reaction involving the treatment of N-silyl-substituted alkyl(aryl)aminoalkylsilanes with chloroformates is more important[2,27,67]:



$$R_3SiCH_2N(SiMe_3)_2+R'OC(O)Cl \rightarrow R_3SiCH_2\overset{\displaystyle SiMe_3}{\overset{|}{N}}C(O)OR'+Me_3SiCl;$$

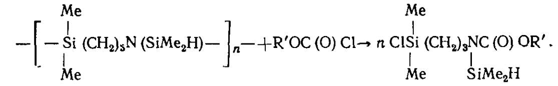
$$kO\left[-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-R-OC(O)Cl\right]_2+kR'\underset{\displaystyle SiMe_3}{N}-[-(CH_2)_n\underset{\displaystyle R'}{N}-]_mSiMe_3 \xrightarrow[n=2,3]{m=1,2;} \rightarrow-\left\{-\overset{\displaystyle O}{\overset{\|}{C}}O-R-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}O\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-R-O-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle R'}{N}-[-(CH_2)_n\underset{\displaystyle R'}{N}-]_m-\right\}_k-;$$

¶ Organic peroxides react with isocyanatoalkylsilanes similarly to alcohols[217]



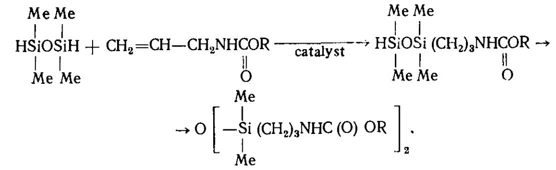
$$(MeO)_3Si(CH_2)_3NCO+HOOCMe_2Ph \xrightarrow[\text{catalyst}]{80^\circ} (MeO)_3Si(CH_2)_3NH\overset{\displaystyle O}{\overset{\|}{C}}OOCMe_2Ph.$$

$$R = -CH_2-,\ -(CH_2)_3-,\ -CH_2O(CH_2)_2-;$$



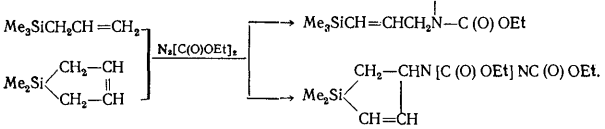
$$-\left[-Si(Me)_2(CH_2)_3N(SiMe_2H)-\right]_n- + R'OC(O)Cl \rightarrow n\,ClSi(Me)_2(CH_2)_3N(SiMe_2H)C(O)OR'.$$

The hydrosilylation reaction, the use of which in the synthesis of *N*-silylorganylurethanes makes it possible to obtain monomeric, oligomeric, and polymeric products with partial or complete blocking of the Si–H bonds by *N*-alkenylurethanes[26,202,221], is of independent importance, for example:



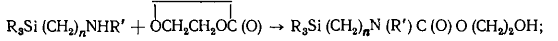
$$HSiMe_2OSiMe_2H + CH_2{=}CH{-}CH_2NHC(=O)R \xrightarrow[\text{catalyst}]{} HSiMe_2OSiMe_2(CH_2)_3NHC(=O)R \rightarrow O\left[-SiMe_2(CH_2)_3NHC(O)OR\right]_2.$$

The interaction of alkenylsilanes with azodiformic acid ester is accompanied by the migration of the double bond of the silane and leads to the formation of a mixture of addition products[222]:



$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{N_2[C(O)OEt]_2} Me_3SiCH{=}CHCH_2N(C(O)OEt){-}C(O)OEt$$

Silicon-containing glycol carbamates are obtained by the aminolysis of alkylene carbonates by alkyl(aryl)aminoalkylsilanes[223,224]:



$$R_3Si(CH_2)_nNHR' + \overline{OCH_2CH_2OC}(O) \rightarrow R_3Si(CH_2)_nN(R')C(O)O(CH_2)_2OH;$$

$$R{=}OAlk,\ Alk;\ n{=}1,3;\ R'{=}H,\ Alk,\ -CH_2CH_2OCH{=}CH_2.$$

The reactivity of γ-amines ($n = 3$) is higher in this reaction than that of α-amines ($n = 1$) and $(Me_3Si)_2NH$ does not undergo this reaction at all.

It has been found that the amides of *C*-silyl-substituted carboxylic acids can be converted into *N*-silylorganylurethanes with retention of the Si–C bonds[225–227]:

$$Me_3Si(CH_2)_nC(O)NH_2 \xrightarrow[n>1]{MeONa/Br_2} Me_3Si(CH_2)_nNHC(O)OMe.$$

2. PHYSICAL PROPERTIES OF SYLYLORGANYLURETHANES

Organosilicon urethanes with carbon-based functional groups are colourless, transparent, mobile, and readily distilled liquids, which have been as a rule characterised by distinct melting points, refractive indices n_D^{20}, densities d_4^{20}, molar refractions MR_D, and infrared and ^1H NMR spectra[2,26,27].

The first amide band in the infrared spectra is in the range 1695–1733 cm^{-1}, as for other organic urethanes[25,26,228], while the second amide band is located in the wider range 1500–1625 cm^{-1}. The stretching vibrations of the free N–H group are manifested by shoulders of low and moderate intensity (3410–3450 cm^{-1}) on the more intense absorption band at 3328–3350 cm^{-1} corresponding to associated groups[25,26]. It is noteworthy that vibrations of the first type due to this group are characteristic of α-substituted urethanes alone. On passing from urethanes with an N–H group to $N{-}SiMe_3$ derivatives, the second amide band vanishes, but an intense absorption appears in the form of two bands at 1348 and 1321 cm^{-1} and there is a simultaneous increase in absorption intensity at 1400–1410 and 1440–1450 cm^{-1}. [25,26]

The ^1H NMR spectra of the urethanes $Me_n(RO)_{3-n}\cdot Si(CH_2)_mNHC(O)OR$, where R = Alk, n = 0 or 3, show the signal of the $N{-}CH_2$ groups split into two independent doublets, which can be explained (by analogy with dimethylformamide) by the double bond character of the linkage between the N and –C(=O)– atoms and the existence of these compounds in the *cis*- and *trans*-forms[26].

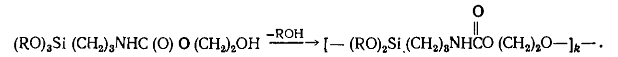
3. CHEMICAL PROPERTIES OF SILYLORGANYLURETHANES

Both *N*- and *O*-silylorganylurethanes with halogeno- or alkoxy-groups at the silicon atom are readily hydrolysed to the corresponding siloxanes[26,31,202]:

$$O[SiMe_2(CH_2)_3NHC(O)OR]_2;$$

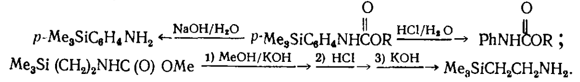
$$O[SiMe_2(CH_2)_3OC(O)NR_2]_2.$$

When acted upon by high-boiling alcohols, they undergo the transesterification reaction[223,224]:



$$(RO)_3Si(CH_2)_3NHC(O)O(CH_2)_2OH \xrightarrow{-ROH} [-(RO)_2Si(CH_2)_3NHC(=O)O(CH_2)_2O-]_k-.$$

Depending on the conditions and the structure of the initial silylorganylurethane, the hydrolysis may involve either the carbamic acid group or the Si–C bond with formation of aminoalkyl(aryl)silanes or desilylation products[209,225,227]:



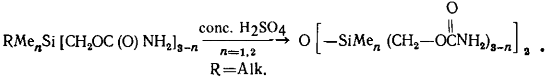
$$p\text{-}Me_3SiC_6H_4NH_2 \xleftarrow{NaOH/H_2O} p\text{-}Me_3SiC_6H_4NHC(=O)R \xrightarrow{HCl/H_2O} PhNHC(=O)R;$$

$$Me_3Si(CH_2)_2NHC(O)OMe \xrightarrow{1)\ MeOH/KOH} \xrightarrow{2)\ HCl} \xrightarrow{3)\ KOH} Me_3SiCH_2CH_2NH_2.$$

The reactions of α- or γ-silylurethanes containing N–H and Si–OAlk groups with $SOCl_2$ proceed only via the Si–O bond[26–28,31,184,228]:

$$ROMe_2Si(CH_2)_nNHC(O)R \xrightarrow[n=1,3]{SOCl_2} ClMe_2Si(CH_2)_nNHC(O)OR.$$

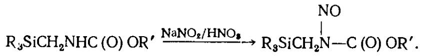
Disiloxanes with two and four urethane groups have been obtained by the Sommer reaction[196]:



$$RMe_nSi[CH_2OC(O)NH_2]_{3-n} \xrightarrow[n=1,2]{\text{conc. } H_2SO_4} O\left[-SiMe_n(CH_2{-}OC(=O)NH_2)_{3-n}\right]_2.$$

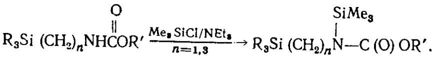
$$R{=}Alk.$$

N-Silylorganylurethanes are nitrosated in accordance with the classical mechanism[220,229]:



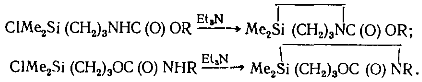
$$R_3SiCH_2NHC(O)OR' \xrightarrow{NaNO_2/HNO_3} R_3SiCH_2N(NO){-}C(O)OR'.$$

On silylation with the Me_3SiCl/NEt_3 mixture, they are converted into disilylurethanes[26,27]:



$$R_3Si(CH_2)_nNHC(=O)OR' \xrightarrow[n=1,3]{Me_3SiCl/NEt_3} R_3Si(CH_2)_nN(SiMe_3){-}C(O)OR'.$$

In many instances the silylation is intramolecular[11,26–28,31,67,184,230,231]:



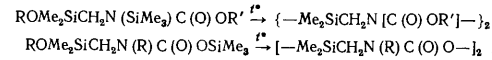
$$ClMe_2Si(CH_2)_3NHC(O)OR \xrightarrow{Et_3N} \overline{Me_2Si(CH_2)_3N}C(O)OR;$$

$$ClMe_2Si(CH_2)_3OC(O)NHR \xrightarrow{Et_3N} \overline{Me_2Si(CH_2)_3OC(O)N}R.$$

The formation of 2,5-disilylpiperazine derivatives is an exception[27]:

$$ClMe_2SiCH_2NHC(O)OR \xrightarrow{Et_3N} \{-SiMe_2CH_2N[C(O)OR]-\}_2.$$

N-Silylated organosilicon urethanes with carbon-based functional groups can undergo *trans*-silylation reactions[22,26–28,67,232,233]:



$$XMe_2Si(CH_2)_3N(SiR_3)C(O)OR' \xrightarrow[X=Cl,\,OR]{t^\circ} \overline{Me_2Si(CH_2)_3N}C(O)OR',$$

$$ROMe_2SiCH_2N(SiMe_3)C(O)OR' \xrightarrow{t^\circ} \{-Me_2SiCH_2N[C(O)OR']-\}_2,$$

$$ROMe_2SiCH_2N(R)C(O)OSiMe_3 \xrightarrow{t^\circ} [-Me_2SiCH_2N(R)C(O)O-]_2.$$

Since the thermolysis of *N*-silylurethanes, like that of other organosilicon urethanes, constitutes a new method for the synthesis of a wide variety of isocyanates and illustrates the theoretically important mechanism of β-decomposition in the ≡Si–N–C–X system of conjugated double bonds, data on this problem are reviewed in the next section.

4. THERMAL DECOMPOSITION OF ORGANOSILICON URETHANES

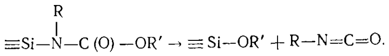
Sufficient data have now accumulated to reach definite conclusions concerning the factors controlling the β-decomposition in the ≡Si–N–C–X (X is an electronegative group) system of σ,σ conjugated bonds[11,12,26,28,31,151,184,230,234,235].

Like their purely organic analogues RNHC(O)OR, *N*-silylorganylurethanes decompose into isocyanates and alcohols on heating to 150–300°C, the decomposition taking place more readily the higher the acidity of the alcohol produced[26,145,186,194,201,218,219,234-238]:

$$R_3Si{-}Q{-}NHC(O)OR' \rightleftharpoons R_3Si{-}Q{-}NCO + R'OH.$$

The reaction is reversible and alcohol is removed from the reaction zone in order to drive it to the right. The reaction then obeys first-order kinetics[194,237].

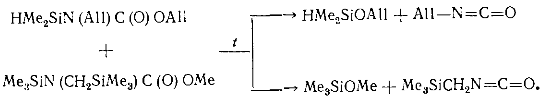
N-Silylurethanes containing the Si–N–C(O)–OR system of conjugated bonds decompose irreversibly on heating into an isocyanate and an alkoxysilane[11,12,20-22,24-28,31,32,36,56,68,142,145,151,184,228,230,232,234-249]:



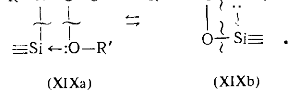
$$\equiv Si{-}\underset{}{\overset{R}{\overset{|}{N}}}{-}C(O){-}OR' \rightarrow \equiv Si{-}OR' + R{-}N{=}C{=}O.$$

With the exception of the special instances discussed below[22,28,31,32,239,241-246], the reaction is irreversible, obeys first-order kinetics, and has $E_{act} = 22$–30 kcal mole^{-1}.

The pyrolysis is intramolecular, which follows from the analysis of the product obtained as a result of the pyrolysis of a mixture of different urethanes[25,27,28,31,240]:



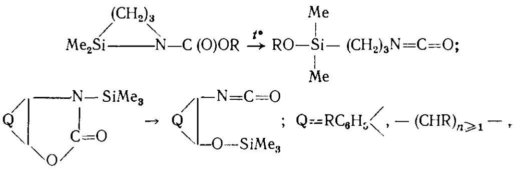
This finding suggests the intermediate formation of the following four-membered transition states involving the amide (XIXa) or imide (XIXb) forms of the *N*-silylurethane[25,26,28,31,230]:



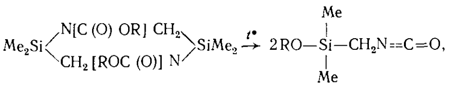
(XIXa) (XIXb)

However, according to the infrared spectra of *N*-silacyclourethanes[22] (the absence of the absorption due to the >C=N bonds at 1540–1640 cm^{-1}) and ^{1}H NMR (the singlet due to the Si–CH$_3$ protons), preference must be given to the amide form (XIXa). The strain in the four-membered transition complex does not rule out this mechanism, bearing in mind the possibility of the intense polarisation of the bonds involved in the electron redistribution[22,28,31,240]. This assumption is confirmed, for example, by the higher reactivity of the Si–N bond in the thermally less stable *N*-silylurethanes in relation to electrophilic agents of the type RC(O)Cl, RC(O)OC(O)R, PhNCO,[22,144], etc.

Depending on the *exo*- or *endo*-location of the ≡Si–N–C(O)–OR atomic group, silacyclourethanes form various β-decomposition products. For example, ring opening takes place in one instance[22,28,29,31,32,184,230,234,239]:

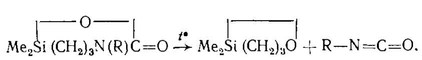


in an other the urethane decomposes into two isocyanate molecules[25,27,28,31,68,142,234]:



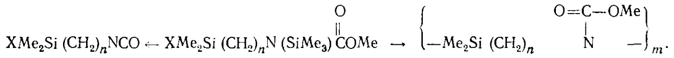
$$Me_2Si\genfrac{}{}{0pt}{}{\diagup N[C(O)OR]CH_2 \diagdown}{\diagdown CH_2[ROC(O)]N \diagup}SiMe_2 \xrightarrow{t^\circ} 2RO{-}\overset{Me}{\underset{Me}{Si}}{-}CH_2N{=}C{=}O,$$

and in the third case, the ring contraction reaction takes place[26,28,31,184,230,234]:



$$Me_2Si(CH_2)_3N(R)C{=}O \xrightarrow{t^\circ} Me_2Si(CH_2)_3O + R{-}N{=}C{=}O.$$

The β-decomposition (D) of the urethanes (XX) is accompanied by the simultaneous *trans*-silylation reaction (T):



	m	n	X	Reaction, %	
				D	T
a	2	1	Cl	0	100
b	2	1	EtO	13	87
c	1	3	EtO	70	30

Evidently the D/T ratio is influenced not only the nature of the substituents at the silicon atom but also by the relative positions of the silyl groups in the urethane molecule[27,28,31,184,232,247]. This is why the study of the kinetics of the β-decomposition of the urethanes $Me_n(MeO)_{3-n}Si(CH_2)_mN.(SiMe_3)C(O)OR$ does not yield a direct answer to the question of the *C*-silyl group on the β-decomposition proper when n varies from 0 to 3.[24-26,184]

The influence of the substituents in the urethanes having the general formula RN(SiMe$_3$)C(O)OR′ on the temperature of the onset of appreciable decomposition is clearly illustrated by the Table below[21,22,25,26,28,29,31,56,68,184,230,250-254].

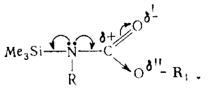
The influence of the substituents R and R′ in the urethanes RN(SiMe$_3$)C(O)OR′ on the temperature of the onset of appreciable decomposition (T_{decomp}).

R	R′	T_{decomp}, °C	R	R′	T_{decomp}, °C
Alk	C_2H_5	170	Ph	C_2H_5	100
Alk	C_6H_5	110	Ph	$N{=}C(CH_3)_2$	60
Alk	C_6H_4Cl-*p*	60	Ph	C_6H_5	20
Alk	$C_6H_4NO_2$-*p*	0	Ph	$C(O)C_6H_5$	0
Alk	Cl	$\leqslant 0$	$SiMe_3$	$SiMe_3$	< 20

The aliphatic oxa(thia)zolidinones $Me_3SiNC(X)OCH(R')C.(R'')H$ (XXI) [a) R′ = R″ = H, X = O; b) R′ = R″ = H, X = S] are converted into isocyanates under more severe conditions (>180°C) than the analogous oxa(thia)azolidine-2,5-diones $Me_3SiN-C(=X)O-C(=O)CHR$ (XXII) and the benzo-derivatives (XXIII) [c) $R' + R'' = C_6H_4$; d) $R' + R'' = 5-MeC_6H_3$; e) $R' + R'' = 5-ClC_6H_3$; X = O throughout], corresponding to the oxa(thia)azolidinones (XXI). The latter compounds form isocyanates at 125–130°C, and the content of the β-decomposition product in the equilibrium mixture decreases in the sequence (XXIIIe) > (XXIIIc) > (XXIIId) and increases with rising temperature and also when it is removed from the reaction sphere[22]. On the other hand, compounds (XXIII) with X = O and $R' + R'' = 4-NO_2C_6H_3$ (f) or $5-NO_2C_6H_3$ (g) do not form isocyanates even at 165°C. [22,28,31,32] For comparison, we may note that *N*-(trimethylsilyl)benzothiazolidin-2-one is stable on heating to 260°C, while its very close analogues *N*-(trimethylsilyl)benzoxalidine-2-thione and 5-nitro-*N*-(trimethylsilyl)-benzoxazolidine-2-thione undergo β-decomposition even in the course of the introduction of silyl protecting groups into the heterocycles[22,239,242,244–246,255]. Furthermore, it is striking that in all cases thiazolidine derivatives show a small tendency towards isomerisation, while silylated oxazolidine-2-thiones rearrange irreversibly and quantitatively and *N*-(trimethylsilyl)oxazolidinones rearrange reversibly[22,239,242,244–246,255].

One may therefore conclude that the thermal stability of *N*-silylurethanes decreases when (a) the electronegativity of the RO group increases, (b) the *N*-alkyl group is replaced by an aromatic group, in particular by a group containing electronegative substituents, (c) on passing from aliphatic *N*-silacyclourethanes to benzo-derivatives, and finally (d) following the introduction of the thiocarbonyl group in place of the carbonyl group[21,22,24–29,31,32,56,68,77,91,142,184,230–234,239,242–256].

Indeed the introduction of an electronegative substituent lowers the basicity of the nitrogen atom as a result of which the amount of double bond character of its linkage with neighbouring Si and C atoms falls:

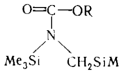


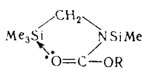
Therefore the β-decomposition reaction involves preferentially compounds containing σ,σ conjugated bond systems $\equiv Si-N-C(O)-OR'$, i.e. in the amide form of the transition complex (XIXa) mentioned above and not in the corresponding imide form $\equiv Si-N=C-OR'$ (XIXb). [26] Experiment confirmed this conclusion: the model compound $MeC(=N-SiMe_3)OEt$ decomposes into MeCN and ethoxytrimethylsilane only above 250°C. [26]

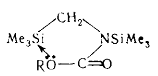
In the light of the foregoing, the instability of $(Me_3Si)_2NC(O)OR$ (decomposition temperature of about 20°C) becomes understandable, since the degree of degeneracy of the basic properties of the nitrogen atom owing to the $(p-d)\pi$ interaction via two Si–N bonds is in this case still greater[56].

The analogous effect of two silyl groups in combination with the high electro-negativity of the NaO^- substituent is the cause of the easy β-decomposition of compounds of the type $(Me_3Si)_2NC(O)ONa$ even in the synthesis of bistrimethylsilylcarbodiimide [88–92].

Furthermore, since the Me_3Si group enhances the nucleophilic properties of the nitrogen atom in the α-position[87], it was to be expected that the thermal stability of the compounds $Me_3SiN(CH_2SiMe_3)C(O)OR$ will be higher than that of $Me_3SiN(Me)C(O)OR$, which, however, conflicts with experiment. The apparent inconsistency is probably a consequence of the superposition of the σ,σ conjugation effects in the $\equiv Si-C-N-C\equiv$, $\equiv Si-C-N-Si\equiv$, and $\equiv Si-N-C-OR$ bond systems or is a result of the transannular interaction of the $C-SiMe_3$ group with one of the oxygen atoms:







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An appreciable decrease of the thermal stability of *N*-silylurethanes is observed not only after the interaction of aryl or silyl substituents at the nitrogen atom but also after the introduction of acyl groups. For example, the acylurethanes $MeC(O)N(SiMe_3)C(O)OMe$ and $PhC(O)N.(SiMe_3)C(O)OMe$ decompose readily at 85–100°C. [257]

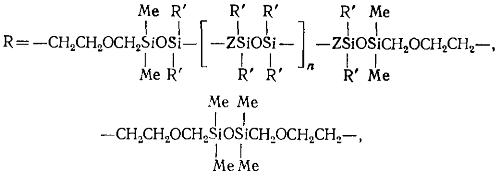
IV. OTHER TYPES OF SILYLURETHANES

This section surveys mainly the available information about systems in which the silicon atom and the carbamic acid fragment are separated by a bridge which does not consist of carbon atoms alone. We have divided the methods for the introduction of silicon into the polyurethane macromolecule into six independent groups†.

1. The polycondensation reactions of a wide variety of monoisocyanates with silicon-containing glycols lead to the synthesis of adducts with terminal urethane groups, for example[260–266]:

$$HO-R-OH + 2R'''NCO \rightarrow R'''NHC(O)O-R-OC(O)NHR''',$$

where



$$R = -CH_2CH_2OCH_2\underset{Me}{\overset{Me}{Si}}O\underset{R'}{\overset{R'}{Si}}-\left[-Z\underset{R'}{\overset{R'}{Si}}O\underset{R'}{\overset{R'}{Si}}-\right]_n-Z\underset{R'}{\overset{R'}{Si}}O\underset{Me}{\overset{Me}{Si}}CH_2OCH_2CH_2-,$$

$$-CH_2CH_2OCH_2\underset{Me}{\overset{Me}{Si}}O\underset{Me}{\overset{Me}{Si}}CH_2OCH_2CH_2-,$$

$R', R'', R''' = $ Alk, Ar; Z = arylene or hydroxyarylene; $n = 0$ or 1.

The replacement of monoisocyanates by di- and polyisocyanates leads to polyurethanes with terminal isocyanato-groups capable of further structure formation[263,267–281]. Polyurethanes with a cross-linked structure are obtained when the structure-forming agent is a polyisocyanate having the biuret structure[275,282–286], as already noted above for organosilicon diols with purely carbon-based functional groups. In practice adducts of 2,4-TDI or 2,6-hexamethylene diisocyanate (2,6-HMDI) with tri(hydroxymethyl)propane are most frequently used as the polyisocyanates and the glycol components consist of ester-alcohols of the series[263,274,275,287–289,302].

Similar products have been obtained from glycols with Si–OC bonds of the general type $R_nSi(OZOH)_{4-n}$ (XXIV) and $Q(SiMe_2OZOH)_2$ (XXV), where R = alkyl or aryl, Z = alkylene, arylene, hydroxyalkylene, or oligohydroxyalkylene, Q = arylene, hydroxyarylene, or oligosiloxane,

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† Since studies on the utilisation of organosilicon compounds in industry and in the processing of polyurethanes (for example as surfactants, stabilisers, pore regulators, etc., i.e. in processes without the obligatory formation of chemical bonds with the polyurethane) are of great practical importance, they merit independent consideration. Certain data on this problem have been reviewed by Adamowski et al. [258] and Zwolinski et al. [259]

and $n = 1-4$.[66,67,113,261-265,274,282,286,290-307] By varying the reactant ratio, the polycondensation process can be arrested in many cases, at the stage involving the formation of the oligomer with terminal hydroxy- or isocyanato-groups, which are responsible for the hardening of prepolymers when suitable reagents are chosen.

2. The condensation reactions of polyethers, which do or do not contain urethane fragments but always have hydroxy-groups in side substituents or at the ends of the chain, with silanes or polysiloxanes containing hydroxy-, alkoxy-, acyloxy-, or amino-groups at the silicon atoms and subsequent condensation of the products with polyisocyanates make it possible to synthesise copolymers with a wide variety of compositions and structures[115,166,180,267,275,290,308-350].

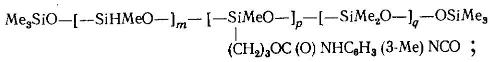
The silicon content in polyurethanes is then regulated by the type and size of the siloxane blocks and their amount in the reaction mixture. In a typical instance of this method, the polysiloxane containing ≡SiOEt groups undergoes transesterification with poly(ethyleneglycol adipate) having terminal hydroxy-groups and is treated with TDI in the presence of a special plastisol composition. Structure formation in the copolymer is completed by heating the mixture at 150°C for 5 min.[322]

Sulphur-containing organosilicon glycols, for example $\alpha\omega$-bis-(β-hydroxyethylthiomethyl)polydimethylsiloxanes, behave in the polycondensation reactions like their oxygen analogues[272,351-353] and in the case of glycols based on diethanolamine, particularly bis-(β-hydroxyethylaminoethyl)dimethylsilane, both N–H and H–O bonds are involved in the reaction[354,355].

3. The hydrosilylation or catalytic dehydrocondensation reactions[222,223,348,356-373] involving polysiloxanes with ≡Si–H bonds and oligourethanes containing C=C and OH groups make it possible to obtain various block-copolymers. For this purpose, oligomers containing free OH or OCN groups are usually treated with the corresponding alkenyl isocyanate or an unsaturated alcohol with subsequent addition of the prepolymer to polysiloxanes with ≡Si–H bonds. Copolymers obtained from silicon-containing glycols or diisocyanates with carbon-based functional groups have similar structures. However, the first version of the synthesis is based on a more readily available starting material[2,26,99-103,368-370,374,375].

The method of synthesising oligourethanes by the reaction of alkyl(aryl)aminoalkylsilanes with chlorocarbonate esters is still less suitable owing to the difficulty of removing the HCl evolved, which causes side reactions[376,377].

Another variety of block-copolymers is obtained by the reaction of $\alpha\omega$-dihydroxy-derivatives of polyesters, polyester-amides, and poly(alkylene glycols) with di- and poly-isocyanates having different ratios of the functional groups ≡Si–H, OH, and OCN to form adducts. The synthesis can involve any of the above groups, for example the isocyanato- or silamethylidyne groups in the polysiloxane[352,355,378,379]:



$$\mathrm{Me_3SiO{-}[{-}SiHMeO{-}]_{\mathit{m}}{-}[{-}\underset{\textstyle |\atop (CH_2)_3OC(O)NHC_6H_3(3\text{-}Me)NCO}{SiMe}O{-}]_{\mathit{p}}{-}[{-}SiMe_2O{-}]_{\mathit{q}}{-}OSiMe_3}\ ;$$

$$m = 2-4.5;\ p = 1-6.5;\ q = 5-22\ ,$$

and the hydroxy-groups in the polyester.

In view of their ready availability and high chemical reactivity, the isocyanates $R_nSi[O(CH_2)_mNCO]_{4-n}$ with R = NCO and particularly with R = H or $CH_2{=}CH$ ($n = 0-2$ and $m \geqslant 1$) may become suitable for the same purposes and may replace glycoxysilanes of type (XXIV)[46,47,380].

Silyl esters of isocyanatocarboxylic acids can also be used to synthesise silicon-containing urethane intermediates[381].

4. Hydrolysis of organosilicon urethanes with SiOR (R = alkyl) and carbon-based functional groups leads to di- and poly-siloxanes containing carbamic acid groups. This property of urethanes is used in the manufacture of polyurethane compositions for cold vulcanisation[2,26,27,382,383].

The low-temperature adducts (XXVI) can harden as a result of hydrolysis involving the SiOMe and OCN groups simultaneously or separately[260,271,273]:

$$\mathrm{REtC(CH_2OH)_2 + TDI \rightarrow REtC{-}[{-}CH_2OC(O)NHC_6H_3(4\text{-}Me)NCO]_2},$$

(XXVI)

where

$$\mathrm{R = (MeO)_3Si(CH_2)_3S(CH_2)_3OCH_2{-},\ (MeO)_3Si(CH_2)_3OCH_2{-}}\ \text{etc.}$$

5. Radical polymerisation reactions are used to a limited extent for the synthesis of polyurethanes[330,339,384-388]. For example, copolymers of $\alpha\beta$-unsaturated urethanes and products of the transesterification of oligosiloxanes with the HO and AlkO terminal groups of acryloyloxy- and methacryloyloxy-derivatives of ester-alcohols, which are hardened by ionising radiation, have been obtained by this method. Styrene is used as a reactive diluent[387,388]. It appears useful to employ in this reaction vinyloxyalkyl and vinylthioalkoxyalkyl carbamates[389].

In the presence of $\alpha\alpha'$-azobisisobutyronitrile, it proved possible to copolymerise vinyltriethoxysilane and 5-methyl-*N*-vinyl-2-oxazolidinone[385].

6. Graft copolymers have been obtained with the aid of the polycondensation reactions already considered from block- or homo-polymers. For example, dyed wear-resistant articles have been obtained by grafting polysiloxane to an organic polyurethane[390-392]. Graft copolymers have been synthesised in which low-molecular weight hydroxylated oligoisoprene and oligobutadiene are linked to a polysiloxane block directly or via a bond system incorporating carbamic acid groups[114,316,393,394].

In another instance hydrated silica (or corundum[388]) is incorporated in polyurethane compositions via a transesterification reaction involving the terminal hydroxy-groups of polyesters [for example, the copolymer of poly(ethylene glycol) and pentaerythrityl adipate] with the corresponding structured tolylene diisocyanate[324,395,396]. It has been shown that polysiloxanes may be grafted to carboranephthalocyanine derivatives[397], thiocol, and $\alpha\omega$-dihydroxypolyfurite [poly(tetrahydrofuran)diol-$\alpha\omega$-bis-(3-hydroxypropane)][180,398], polyamides[59], polyamidourethanes[399], polyamide–polyimides[312], glass[302,317,400], fibreglass[401], leather and poly(vinyl chloride)[269,270,311], derivatives of castor oil and metallocene compounds[402-404], polyester fibres[405-407], and other materials containing different forms of urethane groups.

V. APPLICATIONS

1. *N*- and *O*-Silylurethanes

Like silylated ureas[12], *N*-silylurethanes are used for the treatment of fabrics, paper, leather, cellophane, and other materials in order to make them hydrophobic, reduce their brittleness, impart to them crease resistance, make them electrically insulating, and improve other technical characteristics [13-15]. Organylsilyl tricarbamates $RSi[OC(O)NR'_2]_3$ have been suggested for the low-temperature hardening of organosilicon oligomers with terminal silanol groups [57-59,72].

Although the mode of the reactions of organic diisocyanates with silanediols and oligosiloxanes having terminal OH groups is not always clear, the polymeric products formed are capable of hardening on heating and of giving rise to a film which hardens spontaneously in air [120]; such compounds have a fairly high thermal stability and elasticity [121]. They have therefore been recommended for the preparation of fibres, plastics [104], and for other purposes [97,111,115,128]. In those cases where the principal mode of reaction involves the dehydrocondensation of silanediols [118,122,408], the polysiloxanes formed act as plasticisers on the polymeric ureas produced.

The products of the condensation of $\alpha\omega$-diisocyanatopolyurethanes and polysiloxanes with terminal hydroxy-groups impart to textiles antipilling properties and resistance to shrinking, improve physicomechanical properties, give rise to a pleasant feel, etc., and withstand frequent washing and dry-cleaning as well as prolonged action of light; they also make textiles elastic [117].

Powdered polyurethanes can be pressed into articles with satisfactory electrical insulating properties and high mechanical strength [51,106]. Silyl esters of *N*-alkyl(aryl)-carbamic acids are important intermediates in the synthesis of isocyanates by phosgene-free methods [69,73,77]. The products of the condensation of alcohols with $R_2Si(NCO)_2$ are used to stabilise poly(vinyl chloride). [41] Certain *N*-silylcarbamates exhibit anticholinesterase and insecticidal activities [86,409]. They are isolated in a pure form by a chromatographic procedure [18,19,30].

2. Compounds with Silyl and Urethane Groups Separated by a Bivalent Group

These are extremely numerous and have a wide variety of practical applications. We shall mention some of the most important of these.

Polyurethane film-forming compositions obtained by both cold and hot drying adhere to glass, wood, metals, plastics, and other constructional materials [158,159,162,163,166,183,217,273,287,288,290,292,294,306,307,311,313,316,334,344,352,356,363,373,390,405]. They have a very attractive outward appearance (smooth, transparent, and elastic or solid and lustrous films), are resistant to water, oil, petrol, corrosion, wear, and the atmosphere, their colours are fast, and their useful characteristics are retained under the conditions of high temperatures and humidities. These remarkable qualities have been used in the manufacture of decorative finishing materials [113,168,174,264,265,275,277-282,287-289,298-307,347,409-413].

Various polyurethane compositions are used to treat textile and leather articles in order to make them wear resistant and impart to them dirt-, water-, and oil-repellent properties [161,177,182,212,268,309,310,363,405]. It is important to note that, after treatment, fabrics, paper, and leather articles remain permeable to vapours and gases, are elastic, and are not sticky.

One-component oligopolyurethanes which undergo self-vulcanisation in air are used as cements, fillers, hermetically sealing compounds, gaskets, and shock absorbers in building, automobile, and avaiation industries, and as potting compounds which adhere to glass, wood, porcelain, metals, and plastics. The advantage of coatings based on them (apart from the unique combinations of different types of stability to external influences already mentioned in connection with fancy leather goods and decorative articles) consists also in their capacity to form remarkable gas-filtering and vapour permeable films which are used for encapsulation for the purpose of conservation and storage of specific materials [292,334,352,361,363,367,382-284,405].

In certain cases urethane–siloxane adducts are used as primers which improve the adhesion of polyurethanes to the support [260,271,362,376,377,414], as binders for glass and textile fibres [362], as surface-plasticising coatings [269,270], as electrically insulating articles [222,272,292,315,320-322,325-327,333,334,337,351,358,368,371,372], as sensitisers for heat-sensitive latexes [222,272,315,321,322,327-329,332,333,343,351,358,371,372,403,404,407], as antioxidant additives to anti-detonators [403,404], and as catalysts of the combustion of rocket fuels [348]. Silicon-containing stabilised liquid, semi-liquid, and elastic resins, rubbers, plastics, and other materials with prolonged resistance to water, heat, and fire with retention of geometrical dimensions are manufactured on their basis [59,115,165,183,323,330,331,335,336,342,344,354,355,360,362,378,379,396,415].

The wide variety of the physicochemical characteristics of polysiloxane–polyurethane materials gives rise to the possibility of using them as liquids with very low glass temperatures (down to −125°C) [180,183,190,287,294,296,306,356] and in the form of corundum-filled and mould-hardened grinding discs or other types of abrasive devices [388,416].

Polyurethanes with a siloxane–hydroxyalkylene base can be used as liquid heat exchangers, emulsifiers, wetting agents, lubricants facilitating the removal of articles from moulds, for the formation of completely smooth surfaces of polymers, as well as other purposes [267,269,270,292,334,352,362]. Laminated products used as splinter-proof glass [317], in which the linking element is polyurethane based on an organic oligoisocyanate and an organosilicon polyfunctional alcohol, have been reported.

Compositions comprising silicon-containing products with organic polyurethane materials in which the individual components are not necessarily chemically combined but the formation of chemical linkages via residual functional groups is quite likely and even inevitable under certain conditions, have assumed considerable practical importance [150,161-134,237,259,269,290,308,311,323-327,329-333,338-340,342,345,346,358,364,365,371,372,396,401,406,407,412,416-517].

The siloxane component has become particularly important in the manufacture of polyurethane foam plastics [237,308,326,327,329,331,332,338,340,342,346,358,365,366,371,372,407,419,440-479]. It plays a versatile role which involves a decrease of the surface tension of the system, the emulsification of the reaction mixture (isocyanate–polyester–catalyst), the stabilisation of the foam before its hardening, and the regulation of the structure and size of the cells; at the same time it abolishes the inevitable imbalance between the functional groups of the starting materials without impairing the quality of the polyurethane foam plastic.

However, mechanical mixtures exhibit only a weak stabilising effect, probably owing to the insufficiency and random nature of the chemical linkages between the components of the reaction mixture, which in certain cases complicates the technology owing to the poor compatibility of the individual components and leads to polyurethane foam plastics having inhomogeneous compositions and variable quality [237,338,486,488,489].

Polyester–polysiloxane block-copolymers [237,308,326,327,329,331,332,338,340,342,346,358,365,366,371,372,407], which exhibit a more pronounced stabilising effect, are more compatible. The overall favourable effect is greater the greater the uniformity of the alternation of polyester and polysiloxane blocks in the copolymer[340,485,489]. Under these conditions, the presence of ≡Si–OC groups in the macromolecule is less preferable compared to Si–C bonds[329,331,340,407,464,468,485]. Because of this and the difficulty of synthesising such copolymers, they have been replaced by polysiloxane compounds with free hydroxy-groups attached to carbon atoms[355,485–489], particularly those in which the hydroxyl-containing group is joined to silicon via the ≡Si–C linkage[355,487].

Nevertheless the degree of order among the component macromolecular units and the concentration of OH groups relative to the total number of functional groups of the polyester proved to be insufficient. The preparation of polysiloxane–polyurethane copolymers with rigorously alternating functional groups by the successive introduction into the reaction zone of the diisocyanate, the organic polyester, and the polysiloxane with OH (SH) groups attached to carbon atoms did not solve the problem completely either, since the resulting surface-active substances contained only random chemical linkages with the main polymeric mass.

The optimal version of this synthesis now provides for the use of organosilicon oligoisocyanates with carbon-based functional groups in a pure form or in combination with organic di- or poly-isocyanates. After such a substance is brought into contact with an organic polyester, a homogeneous, high-quality, self-stabilising system is produced. The use in the synthesis of organosilicon alcohols, glycols, isocyanates, etc. with carbon-based functional groups as part of the glycol or isocyanate components of the reaction mixture made it possible to obtain, as already described above to some extent, polyurethanes with an exceptionally favourable combination of technically useful characteristics[159,162,309,355,409,412,518–523].

Monomeric derivatives of carbamic acid are used as additives which improve the properties of polysiloxane lubricants for high-temperature high-speed bearings[492], as dispersing additives improving the thickening capacity of silica gel in the manufacture of greases[493], for the vulcanisation of silicone rubbers[27,494–496], and for other purposes[26,497–499].

The widely variable physiological activity of organosilicon urethanes is striking[81,86,153,166,178,193,195–198,204,362,386,399,402,409,524–527].

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Chemical Degradation of Polymers in Corrosive Liquid Media

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The physicochemical foundations of the degradation of polymeric materials in corrosive liquid media are examined and the characteristics of the polymer degradation processes, the mechanisms of reactions of chemically unstable bonds, and the principal types of decomposition of polymeric molecules as well as the characteristics of the diffusion of corrosive media into polymeric materials are discussed. Kinetic equations have been obtained for the principal types of chemical degradation of polymeric materials under heterogeneous conditions.
The bibliography includes 86 references.

CONTENTS

I. INTRODUCTION

As a result of the wide-scale application of polymers in the chemical and petrochemical industries, in medicine, in the building industry, and in various branches of modern engineering, much attention has been devoted to their degradation processes in corrosive media. In many instances these processes are undesirable, because they lead to loss of valuable practical properties of polymeric articles. In other cases they are used for numerous chemical transformations, the etching of polymers, the dissipation of polymers in living organisms, etc.

The problems of the chemical stability of polymers have been the subject of numerous investigations, but the latter have not as a rule involved a theoretical analysis of the experimental data and are in many instances empirical in nature. The inadequacy of the theoretical studies in the field of chemical degradation of polymers and the availability of a large amount of experimental data make it necessary to discover quantitative relations in the first place.

Corrosive media can be divided into two groups in terms of the type of their action[1,2]:

1. Physically corrosive media giving rise to reversible changes in the polymer.
2. Chemically corrosive media (acid–base and oxidative) under the influence of which the polymer undergoes irreversible changes†.

Naturally, certain media (for example many organic acids) can behave simultaneously as both physically and chemically corrosive media.

Concepts such as chemical ageing, corrosion, chemical degradation, and longevity of the material are nowadays used in the literature and in standards[2] to characterise the decomposition of polymeric materials under the influence of corrosive media.

The term "ageing" was taken from biology and is widely applied in science and engineering. The ageing of polymers is understood as the set of physical and chemical processes occurring in the polymer in corrosive media and giving rise to changes in the properties of polymeric materials. These changes usually lead to the impairment of the practical properties of the polymer.

The term "corrosion" was borrowed from metals science; chemical corrosion of metals is understood as the interaction of the metallic surface with the surrounding corrosive medium. The decomposition of polymeric materials in corrosive media usually occurs in a reaction zone the size of which may vary from several monolayers to the entire bulk of the polymeric article. Therefore the term "corrosion" as applied to polymers is too narrow and cannot be recommended.

Chemical degradation is usually understood as all the processes leading to a change in the chemical structure of polymeric materials. Thus chemical degradation constitutes the set of the following chemical processes occurring in the polymer in corrosive media and altering its molecular weight:

(a) depolymerisation—the abstraction of the monomer from the end of the macromolecule;

(b) polymer-analogue decomposition of the monomer—the abstraction of a group of atoms from the macromolecule with retention of the initial degree of polymerisation;

(c) decomposition of the main chain leading to a decrease of the degree of polymerisation;

(d) cross-linking—reactions involving the formation of chemical bonds between the macromolecules and leading to the appearance of branched and network structures.

The chemical degradation of polymers under the influence of oxidants is a complex process including, as a rule, radical, molecular, and ionic chemical reactions; degradation under the influence of acids and bases consists largely of hydrolytic, solvolytic, or abstraction reactions.

The criteria of the chemical resistance of polymeric materials to the action of corrosive media have been defined in a number of standards[2]. Longevity should be understood as the period during which the properties of the polymeric material change under particular conditions of its employment to the level specified in the technical documentation.

The study of the kinetics of chemical degradation is extremely difficult both as regards the determination of

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† Biochemical media are also included here.

correct experimental data and the determination of the kinetic parameters of the individual fundamental steps. For a successful solution of this problem, it is necessary to discover in the first place whether the chemical degradation process can be resolved into a series of simpler processes (for example diffusion of the corrosive medium into the polymer and chemical reaction of the functional groups) in order to investigate them separately; secondly, one must find out to what extent these processes can be simulated using low-molecular-weight analogues. Such simulation is necessary, because one cannot always separate the chemical reaction step from diffusion phenomena and, furthermore, it is always interesting to compare the calculated kinetic and diffusion parameters of the chemical degradation process with the corresponding parameters of model processes.

The aim of the present review is to examine the physicochemical foundations of the degradation of polymeric materials in corrosive media, whereby one can characterise the chemical degradation process in terms of kinetic and diffusion parameters and to predict the chemical stability of polymeric materials under the conditions of their employment. We do not aim to quote all the known facts and data concerning the chemical degradation of polymers. An attempt has been made in the review to examine at a quantitative level the degradation processes of polymeric materials in corrosive media. The review deals mainly with the degradation of polymers under the influence of acids and bases, which is most frequently encountered in practice.

II. THE CHARACTERISTICS OF POLYMER DEGRADATION PROCESSES

Flory[3] formulated the main principles of the independence of the reactivities of the functional groups in oligomers and polymers of molecular weight for various types of reactions. The functional groups in the polymer must have the same reactivities as in a low-molecular-weight model compound when the following conditions are observed:

(a) the reaction proceeds in a homogeneous medium in which the initial reactants and products are soluble;

(b) one type of functional group of the polymer is involved in each fundamental step, and the molecules of all the remaining reactants are small and fairly mobile;

(c) the low-molecular-weight analogue is chosen taking into account the steric hindrance which may arise when the conformation of the macromolecule changes during the reaction.

Alfrey[4] noted that identical reactivities of the functional groups in the polymer and in the low-molecular-weight analogue may be observed even if one of the above conditions does not hold.

However, many instances are now known where the reactivities of various groups in the polymer are anomalous owing to the specific influence of the polymeric state[5-7]. We shall consider for simplicity the homogenous catalytic degradation of a polymer via the following mechanism:

$$\sim R + \mathrm{Cat} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \sim X; \qquad \text{(I)}$$

$$\sim X + R' \xrightarrow{k_3} P + \mathrm{Cat}, \qquad \text{(II)}$$

where R is a functional group in the polymer, Cat the catalyst, X an intermediate state, R′ a reactant (for example H_2O in hydrolysis), and P the reaction product.

The viscosity of polymer solutions may be several orders of magnitude greater than that of solutions of low-molecular-weight analogues; furthermore, the functional groups in polymers are as a rule distributed close to one another. Therefore, in comparing the reactivities of the group R in the polymer and in the low-molecular-weight analogue (chosen taking into account the steric hindrance arising during the change in the conformation of the macromolecule during the reaction), one must elucidate the influence of the macroviscosity of the solution and of the interaction of the functional groups on the degradation reactions (I) and (II).

1. A QUANTITATIVE ESTIMATE OF THE INFLUENCE OF THE MACROVISCOSITY OF THE SOLUTION ON THE DEGRADATION KINETICS

The influence of the macroviscosity of the solution on the kinetics of the degradation of small molecules has already been examined[8-10]. If, for example, the rate of the reaction of R with Cat is high compared with the rate diffusion of Cat to R, then the concentration of Cat in the immediate vicinity of R may be reduced, which creates a concentration gradient causing a diffusional flux of the species directed towards R. In the steady state the velocity of this flux becomes equal to the rate of the reaction of R with Cat. According to Plate[6], we obtain

$$k_{\mathrm{eff}} = \frac{4\pi\rho D k_{\mathrm{true}} \cdot \beta}{k_{\mathrm{true}} + 4\pi\rho D\beta}, \qquad (1)$$

where k_{eff} and k_{true} are respectively the effective and true rate constants, ρ is the distance between the centres of the reacting species, β a proportionality coefficient having the dimension molecule^{-1}, and D the diffusion coefficient of Cat or the reactant R′ in the medium. One should note that, even when the functional group in the polymer completely lacks mobility, the frequency of the collisions of R with Cat does not change significantly.

Conditions governing the reaction in kinetic or diffusion regions can be readily obtained from Eqn. (1):

when $k_{\mathrm{true}} \ll 4\pi\rho D\beta$, $k_{\mathrm{eff}} = k_{\mathrm{true}}$,

i.e. there is an equilibrium statistical distribution of the species in solution (the kinetic region of the reaction);

when $k_{\mathrm{true}} \gg 4\pi\rho D\beta$, $k_{\mathrm{eff}} = 4\pi\rho D\beta$,

i.e. there is a sharp breakdown of the equilibrium statistical distribution of the species in solution (diffusion region of the reaction).

At the usual temperatures in non-viscous media, we have $D_{\mathrm{cat}} \simeq 10^{-6}-10^{-5}$ cm^2 s^{-1} (Table 1) and the values of ρ for typical functional groups and catalysts amount to seversl angstroms. Consequently, $4\pi\rho D\beta \simeq 10^{-12}-10^{-11}$ cm^3 mol.$^{-1}$ s^{-1} or 10^9-10^{10} litre mole^{-1} s^{-1}. Thus reactions with $k_{\mathrm{true}} > 10^8$ litre mole^{-1} s^{-1} occur in the diffusion region. The reactions of the proton, the hydroxide, ion[9], and enzymes[10] with the functional groups of the reactants, i.e. stage (1) of the polymer degradation process, do in fact occur in this region.

The rate of reactions with $k_{\mathrm{true}} < 10^8$ litre mole^{-1} s^{-1} is not limited by diffusion and such reactions occur in the kinetic region. These include the decomposition of the ionised forms of the functional groups and of the majority of enzyme–substrate complexes involving the formation of the reaction products [stage (II) of the polymer degradation process]. In the majority of cases the rate of this stage limits rate of the entire degradation process. On passing to viscous systems, ρ hardly changes, while D decreases with increase of the viscosity of the system. For example, D changes with increase of the viscosity of electrolyte solutions in accordance with the equation[11]

$$D = D_0\left(\frac{\eta_0}{\eta}\right)\left(1-\frac{e^2q}{4\epsilon kT}\right), \tag{2}$$

where D_0 and η_0 are the diffusion coefficient and the viscosity at infinite dilution respectively, e is the electronic charge, ϵ the dielectric constant of the medium, q a variable quantity which depends on the electrolyte concentration, and k the Boltzmann constant.

Table 1. Diffusion coefficients of acids in water.

Catalyst	$10^6 D_{25°}$, $cm^2\ s^{-1}$	References
HCl	30.0	13
H_2SO_4	12.0	11
H_3PO_4	8.7	14

It is noteworthy that Eqn. (2) is inapplicable to very viscous media. In solid polymers, $D_{25°} \simeq 10^{-9}-10^{-8}$ $cm^2\ s^{-1}$ for water[12] and $4\pi\rho D\beta \simeq 10^5-10^6$ litre $mole^{-1}\ s^{-1}$. These data lead to the conclusion that, even in very viscous media (solid polymers), the rate of state (II) is not limited by diffusion, i.e. this stage occurs in the kinetic region (we have in view a microkinetic treatment in contrast to a macrokinetic treatment, to which the last part of the review is devoted).

Thus the macroviscosity of the reaction medium influences significantly the rate of reaction between catalysts and the functional groups of the reactants and has almost no effect of the decomposition of the complexes of the functional groups with catalysts, resulting in the formation of products. On the other hand, in most cases the latter reaction in fact constitutes the rate-limiting stage of the entire degradation process.

2. A QUANTITATIVE ESTIMATE OF THE INFLUENCE OF THE INTERACTION OF FUNCTIONAL GROUPS ON THEIR REACTIVITY IN THE POLYMER

If the functional groups in the polymeric molecules are distributed at distances which virtually rule out their mutual influence, then the kinetic parameters of the degradation reactions of polymers and their low-molecular-weight analogues are similar, i.e. the principle of independence of reactivity of molecular weight is valid. Table 2 lists the kinetic parameters for the degradation of polymers and their low-molecular-weight analogues; within the limits of experimental error, these parameters are similar. It is interesting to note that the reactivity (k_{eff}) of acrylic polymers in the H–D exchange reaction is approximately two orders of magnitude lower than that of the corresponding low-molecular-weight analogues (Table 3); according to Scarpa et al.[21], this is due to the decrease of the dissociation constant of water near amide groups relative to the solution.

However, functional groups are frequently distributed close to one another (at distances <10 Å) and this is in fact the cause of the anomalous reactivity of the functional groups in polymers. The following types of the anomalous reactivity of the functional groups in polymers have been distinguished: (a) the effect of an adjoining group which may be either of the long-range type (the "chain effect") or of the short-range type (i.e. the influence of groups located in the immediate vicinity of the given functional group); (b) conformational effects—effects due to the change in reactivity caused by the changes in the form of the macromolecule in the given reaction medium or in the course of the reaction.

Table 2. Kinetic parameters of the degradation reactions of polymers and their low-molecular-weight analogues.

Polymer and its low-molecular-weight analogue	Solvent-catalyst	$k_{true}(25°)$, s^{-1}	E, kcal $mole^{-1}$	lg A* (s^{-1})	References
Polycaproamide	$H_2O—H_2SO_4$	$8.3\cdot10^{-8}$	20±1	7.2	15
Cyclic caprolactam trimer		$8.3\cdot10^{-8}$	20±1	7.4	
Cellulose	$H_2O—HCl$ $H_2O—H_2SO_4$ $H_2O—HClO_4$ $H_2O—H_3PO_4$	$1.1\cdot10^{-8}$	30±1	14.2	16
Cellobiose		$1.6\cdot10^{-8}$	30±1	14.0	
Poly-*NN*-diethylacrylamide	H_2O— buffer	$2.5\cdot10^{-7}$ $(3.1\cdot10^{-9})$	22.0 (24.6)	9.5 (9.5)	17
NN-Diethylisobutyramide		$2.0\cdot10^{-7}$ $(8.0\cdot10^{-9})$	21.7 (23.7)	9.1 (9.5)	(18)
Polyacrylamide	»	$2.0\cdot10^{-5}$	14.2	5.6	19
Isobutyramide		$2.0\cdot10^{-5}$	14.2	5.6	
Poly-*N*-vinyl-2-pyrrolidinone	»	$3.1\cdot10^{-7}$	25±1	11.7	20
N-Isopropyl-5-methyl-2-pyrrolidinone		$4.0\cdot10^{-8}$	27±0.5	12.3	

*A = pre-exponential factor.

Table 3. Kinetics parameters of the H–D exchange reaction in polymers and their low-molecular-weight analogues.

Polymer and its low-molecular-weight analogue	Solvent-catalyst	$k^*_{true}(25°)$, s^{-1}	E, kcal $mole^{-1}$	lg A (s^{-1})	Refs.
Polyisopropylpropionamide	$D_2O—DCl$	$5.0\cdot10^{-5}$	20.0	10.3	21
N-Isopropylpropionamide	$D_2O—KOD$	$2.5\cdot10^{-3}$	20.0	12.0	
Poly-*N*-aminomethacryloyl-L-lysine	—	$6.6\cdot10^{-5}$	19.0	9.8	22
ϵ-Aminoisobutyryl-L-lysine		$2.5\cdot10^{-3}$	16.0	9.1	
Polymethylpropionamide	—	$4.0\cdot10^{-4}$	18.0	9.7	23
N-Methylacetamide		$1.0\cdot10^{-2}$	17.0	10.4	

*The rate constant at the minimum in the relation between lg k_{eff} and pD.

These effects can probably be accounted for by polar, resonance, and steric effects[24], which are well known in organic chemistry, just as the mechanism of the hydrolytic action of chymotrypsin has been explained with the aid of explicit chemical analogues[25].

a. The Long-range Effects of Neighbours of the Group

As a rule, this effect is illustrated by comparing the reactivities of monomers having a system of conjugated double bonds and of a model compound having a single double bond. We shall consider the manifestation of the chain effect in the dehydrochlorination of poly(vinyl chloride) (PVC) at high temperatures. The dehydrochlorination process is known to occur in steps, the double bonds formed activating the next dehydrochlorination step (allylic activation). An attempt has been made[26] to subdivide the complex dehydrochlorination process into two reactions: (1) the random formation of isolated double bonds and (2) the growth of the system of conjugated bonds as a result of allylic activation.

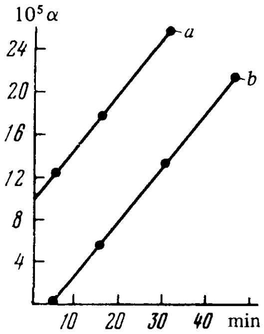


Figure 1. The rate of dehydrochlorination of PVC (*a*) and chlorinated PVC (*b*) at 175 °C; α is the number of breaks per mole of the polymer[26].

Fig. 1 presents the rates of dehydrochlorination of PVC (a) and chlorinated PVC (b) at 175 °C. Evidently the formation of isolated double bonds is independent of the nature of the PVC specimen and proceeds at the same rate ($k_1 = 8.6 \times 10^{-8}$ s^{-1}). In the general case the overall PVC dehydrochlorination process can be described by the following equation without taking into account the destruction of kinetic chains in the initial stages:

$$\frac{\mathrm{d}[\mathrm{HCl}]}{\mathrm{d}t} = k_1 + k_2 X_t,$$

where $k_2 = (W_{\mathrm{PVC}} - W_{\mathrm{CPVC}})/X_0 = 9.3 \times 10^{-4}$ s^{-1}, W_{PVC} and W_{CPVC} are the rates of dehydrochlorination of PVC and chlorinated PVC respectively, and X_0 and X_t are respectively the numbers of double bonds in PVC at the initial instant and at time t.

Table 4. Kinetic parameters of the dehydrochlorination reaction of model compounds for PVC in the gas phase[27].

Model compound	Temp. range, °C	$10^{11}k_{117°}$, s^{-1}	E, kcal mole^{-1}	lg$A$
2-Chlorobutane	347—394	3.6	49	13
2,4-Dichloropentane	347—397	3.3	49	13
2,4,6-Trichloroheptane	346—386	3.4	51	14
4-Chloropent-2-ene	296—345	859	41	12
6-Chlorohepta-2,4-diene	302—347	45 900	35	10
3-Chloropent-1-ene	319—380	8.9	51	15

It is interesting to compare the constants obtained with the results[27] for compounds simulating PVC (Table 4).

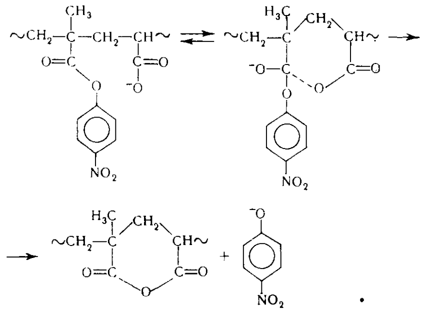
The presence of a double bond at the end of the macromolecule does not have an appreciable influence on the dehydrochlorination reaction (3-chloropent-1-ene); the double bond in the 2- or 4-position greatly accelerates the dehydrochlorination reaction and 4-chloropent-2-ene and particularly 6-chlorohepta-2,4-diene can simulate the allylic activation effect. It is noteworthy that the rate constant for the dehydrochlorination of the latter compound is 10^4 times higher than the rate constant for alkyl chlorides.

Thus the formation of isolated double bonds and the growth of the system of conjugated bonds as a result of allylic activation can be simulated by the dehydrochlorination reactions of alkyl chlorides and 6-chlorohepta-2,4-diene respectively.

b. The Short-range Effect of a Neighbouring Group

Effects of this type occur when the substituent adjoining the given functional group favours or hinders the formation of the activated complex.

For example, the hydrolysis of the copolymer of acrylic acid and *p*-nitrophenyl methacrylate proceeds more readily than that of *p*-nitrophenyl acetate, since in the former case a six-membered activated complex is formed easily following the attack by the carboxylate ion on the ester linkage[28]:



(III)

At 0 °C and pH 6 the rate constants for the intramolecular (copolymer of acrylic acid and *p*-nitrophenyl methacrylate) and intramolecular (*p*-nitrophenyl acetate or acetate ion) hydrolysis are respectively 2×10^{-3} s^{-1} and 6.5×10^{-7} litre mole^{-1} s^{-1}.

The question of the influence of neighbouring groups on the given functional group has been examined theoretically[29-35]. Functional groups of three types may be present in a polymeric molecule under the conditions of a low degree of conversion:

1) groups whose nearest neighbours have not reacted;
2) groups having one neighbour which has reacted;
3) groups having two neighbours which have reacted.

The rates of reaction of functional groups under the conditions of an excess concentration of the catalyst are defined by the equation

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k_0 N_0 + k_1 N_1 + k_2 N_2,$$

where k_0, k_1, and k_2 are respectively the rate constants for reactions of type 1, 2, and 3 functional groups and N_0, N_1, and N_2 are the mole fractions of the corresponding types of functional groups. The solution of the system of the corresponding differential equations relating the change in N_n of a sequence of n groups which have reacted to the corresponding concentrations of functional groups of different types, the rate constants, and time leads to the following expressions[29]:

$$N_0 = \exp\left\{-\left(2\frac{k_1}{k_0}+1\right)k_0t - 2\left(\frac{k_1}{k_0}-1\right)[(\exp - k_0t) - 1]\right\};$$

$$N_1 = [\exp k_0t - 1]\exp\left\{-\left(2\frac{k_1}{k_0}+1\right)k_0t - 2\left(\frac{k_1}{k_0}-1\right)[(\exp - k_0t) - 1]\right\}.$$

The solution for N_2 is complex: for example, when $k_1/k_0 = 1$, we have

$$N_2 = \frac{2}{\left(\frac{k_2}{k_0}-2\right)\left(\frac{k_2}{k_0}-3\right)}\left[\left(\frac{k_2}{k_0}-3\right)\exp(-2k_0t) - \left(\frac{k_2}{k_0}-2\right)\exp(-3k_0t) + \exp(-k_2t)\right].$$

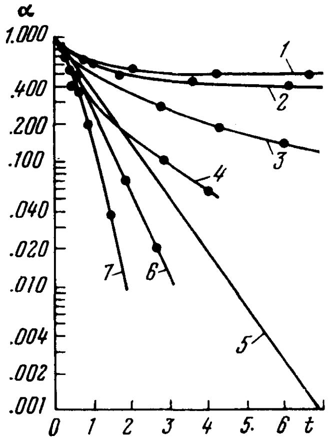


Figure 2. Variation of the degree of conversion of the functional groups in the polymer with time for different reaction rate constants[31]; respective values of the rate constants k_0, k_1, and k_2: 1) 1.0, 4×10^{-2}, 4×10^{-4}; 2) 1.0, 0.2, 1×10^{-2}; 3) 1.0, 0.5, 0.2; 4) 1.0, 1.8, 0.5; 5) 1.0, 1.0, 1.0; 6) 1.0, 1.8, 1.5; 7) 1.0, 2.0, 5.0.

Fig. 2 illustrates the variation of the degree of conversion of the functional groups in the polymer with time for different reaction rate constants obtained by Arends[31]:

$k_0 = k_1 = k_2$ (linear relation),
$k_0 = 1,\quad k_1 < 1,\quad k_2 < 1$ (self-inhibition),
$k_0 = 1,\quad k_1 > 1,\quad k_2 > 1$ (self-acceleration).

The second case, where the degradation process does not reach completion owing to self-inhibition, i.e. there is a certain limiting degree of conversion, is encountered most frequently. A statistical approach to the solution of this problem has been adopted[31-33].

The limiting degrees of conversion of functional groups in the polymer (α) for different ratios k_0/k_1 are listed below[35]:

α	0,667	0,632	0,606	0,600	0,586	0.577	0,50
$\frac{k_1}{k_0}$	1	0,5	0,25	0,20	0,10	0.05	0,01

The kinetics of the alkaline hydrolysis of polyacrylamide have been thoroughly investigated in the same study[35]. In order to describe the experimental data, the authors made the mechanism more involved by assuming that the carboxylate group formed can influence not only the neighbouring group but also the next amide group. They quote the following data for the influence of the carboxylate groups on the reactivity of the amide linkages in the alkaline hydrolysis of polyacrylamide at 60°C:[35]

	—A—A—A—	—A—A—C—A—A—	—C—A—A—C	—C—A—C—
10^4k, litre mole^{-1} s^{-1}	10.8	3	2	0.05
$\Delta G^{\neq}$, kcal mole^{-1}	0	0.7	1 0	3.0

A = amide group, C = carboxylate group

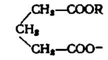
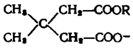
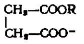
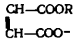
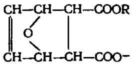
The increase of the free energy of activation owing to the influence of the neighbouring carboxylate groups was determined from the formula

$$\Delta G = \frac{e^2R}{\varepsilon\cdot\bar{r}\cdot k},$$

where R is the gas content and $\bar{r}$ the average distance between the amide linkage and the carboxylate group, assumed to be 3.5 Å.

When the effect of a neighbouring group is considered, it is important to discover (a) what changes in the reactivity of the given functional group may be expected as a result of its approach to the neighbouring functional group, and (b) the mechanism of the action of the neighbouring functional groups. We shall consider as an example the intramolecular alkaline hydrolysis of monophenyl esters of dicarboxylic acids[36,37].

Table 5. The influence of structure on the reactivity of monophenyl esters of dicarboxylic acids in the intramolecular hydrolytic reaction in an alkaline medium[36,37].

No.	Reactants	Relative rate constant
I		1.0
II		20
III	 $\begin{array}{l}CH_2{-}COOR\\ \vert\\ CH_2{-}COO^-\end{array}$	230
IV	 $\begin{array}{l}CH{-}COOR\\ \Vert\\ CH{-}COO^-\end{array}$	10 000
V	 R = C_6H_5 or p = BrC_6H_4	53 000

The data presented in Table 5 show that the bicyclic compound (V) reacts 53 times faster than monophenyl glutarate (I), i.e. in a series of low-molecular-weight compounds it is possible to attain greater differences between reactivities than in the example quoted above.

The intramolecular reactions cannot be accelerated by the following factors[38,39]:

(a) A local increase of the concentration of reactant near the bond being hydrolysed during the intramolecular reaction. For example, the effective concentration of carboxylate groups near the ester linkage in the hydrolysis of the copolymer of acrylic acid and p-nitrophenyl methacrylate may be estimated from the ratio $k_{\text{intramol.}}/k_{\text{intermol.}}$. It amounts to 3×10^3 mole litre^{-1}, which is much larger than the concentrations actually reached.

(b) A favourable mutual orientation of the reacting groups, since the kinetic differences between the intramolecular and intermolecular reactions cannot be reduced to the entropy effect alone.

Changes in solvation can make a considerable contribution to the acceleration of certain intramolecular reactions (including "polymerisation" reactions). For the formation of the activated complex via the intramolecular hydrolytic reaction of monophenyl esters of dicarboxylic acids, it is necessary that the water molecules hydrolysing the charged carboxylate group should be removed. Examination of molecular models shows that in the ester (V) this group cannot be hydrated by water on the side where the ester linkage is attacked. Therefore, during the above intramolecular reaction, energy is not required for the removal of water from the hydration shell.

It is also possible to draw the following analogy. The catalytic properties of the proton, expressed in terms of the acidity function, increase as water molecules are eliminated from its hydration shell. In non-aqueous solvents, for example acetic acid, nitromethane, and sulpholane, the acidity function is several orders of magnitude higher than in aqueous solution at the same sulphuric acid concentration[40]. These effects are probably the cause of the high rates of intramolecular reactions in both polymers and in their low-molecular-weight analogues.

c. Conformational Effects

Depending on the temperature and the composition of the solution, the macromolecules can exist in different conformations where the functional groups differ in reactivity. This is associated with the change in the relative disposition of the functional groups and in addition with their different accessibilities to the external reactant. This case obtains in the alkaline hydrolysis of polyacrylamide, where the formation of carboxylate groups leads to a transition of the macromolecule from the globular to the uncoiled form; unfortunately a kinetic assessment of this effect has not been made. Similar effects are characteristic of polymeric molecules with a pronounced secondary structure (polypeptides, polyorganosiloxanes, etc.).

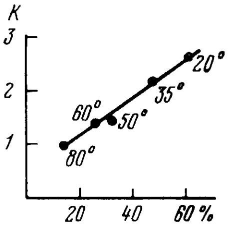


Figure 3. Variation of the ratio of the rate constants for the $^1H \rightarrow {}^3H$ exchange reaction involving AMP and poly-A with the fraction of bases in poly-A participating in the stacking interaction[41].

The $^1H \rightarrow {}^3H$ exchange reaction has been investigated in polyriboadenylic acid (poly-A) and its low-molecular-weight fragment—adenosine 5-monophosphate (AMP)—at pH 7.1.[41] In neutral solutions below 0°C, the poly-A molecules have the conformation of rigid rods consisting of helices of the same type. The stabilisation of these helices is determined primarily by the stacking interaction via the π electrons of the purine rings and hydrogen bonds. With increase of temperature, the interaction between the bases weakens and the polymer molecules become more labile. The AMP molecules retain their structure at all temperatures.

Fig. 3 illustrates the variation of the ratio K of the rate constants for the $^1H \rightarrow {}^3H$ exchange reaction involving AMP and poly-A with the fraction of the bases in poly-A participating in the stacking interaction. The latter quantity was determined by an independent procedure. The observed proportionality between K and the fraction can be regarded as evidence that the stacking interaction causes the retardation of the exchange of hydrogen atoms in the C–H bonds of the adenyl residues.

Thus the anomalous reactivity of "polymeric" functional groups, caused by the primary structure (the short- and long-range effects of the neighbouring group), can probably be determined and simulated with the aid of low-molecular-weight analogues. The anomalous reactivity caused by the secondary structure (conformational effects) is specific to the polymeric state.

III. THE MECHANISMS OF REACTIONS OF CHEMICALLY UNSTABLE BONDS OF VARIOUS POLYMERS IN CORROSIVE MEDIA

Solutions of acids and bases catalyse chemical degradation reactions of monomers. By the mechanism of the catalytic action of acids and bases, we mean the set of data concerning the equilibrium between the ionised and unionised forms of the substance in the reaction medium and the mechanism of the slow fundamental stages limiting the rate of the process.

1. THE MEASURE OF THE CATALYTIC EFFECT OF CORROSIVE MEDIA

The catalytic effect of acids and bases is usually estimated in terms of the capacity of the medium to behave as a donor of protons or hydroxyls. In dilute aqueous solutions of acids and bases, the pH may serve as a quantitative measure of the catalytic effect. However, at electrolyte concentrations in excess of 0.1 M the deviation from ideal solutions becomes appreciable, so that a rigorous quantitative determination of the activity of the proton or the hydroxyl becomes impossible. Hammett[42] proposed an empirical approach to the determination of the acidity of solutions of acids with the aid of indicators.

For the protolytic equilibrium

$$\mathrm{In} + \mathrm{H}^+ \rightleftarrows \mathrm{InH}^+ ,$$

the dissociation constant of the conjugate acid of the indicator InH^+ can be expressed as follows:

$$K_{\mathrm{InH}^+} = \frac{a_{\mathrm{H}^+} f_{\mathrm{In}}}{f_{\mathrm{InH}^+}} \cdot \frac{c_{\mathrm{In}}}{c_{\mathrm{InH}^+}} ,$$

where a is the activity, f the activity coefficient, and c the concentration. The concentrations of the ionised and unionised forms of the indicator are determined spectrophotometrically. Knowing K_{InH^+}, the quantity

$$h_x = a_{H^+}\frac{f_{In}}{f_{InH^+}}, \tag{3}$$

called the acidity of the medium, can be calculated. By analogy with pH, the acidity function is $H_X = ph_X$. More than ten acidity functions, defined with the aid of different classes of indicators, are now known and according to Hammett none of them have any advantages over the others[43].

Thus, since the acidity is determined not only by the capacity of the medium to give up protons but also by the capacity of the indicators to combine with protons, the absolute acidity of the medium cannot be determined by the indicator method, although definite progress has been made in this field during recent years.

Yates et al.[44] calculated a_{H^+} for aqueous solutions of sulphuric and perchloric acids by Eqn. (3) and the activity coefficients were determined by the solubility method. The values of a_{H^+} thus obtained agree with the results determined by electrochemical methods using the ferrocene–ferrocenium system as the reference electrode. Several alkalinity functions are also known for solutions of bases[45,46].

2. CLASSIFICATION OF THE MECHANISMS OF HYDROLYSIS

The mechanisms of the hydrolysis of various compounds have been classified by Ingold[47] on the basis of two main features:

1. Type of catalysis (A—acid, B—base).
2. The molecularity of the rate-limiting stage.

We shall consider the principal relations for uni- and bi-molecular processes.

A. The Unimolecular Mechanism

Consider a reaction via the mechanism

$$R + Cat \overset{K_X}{\rightleftarrows} X;$$

$$X \rightleftarrows M^{\neq} \xrightarrow{k_{true}} P + Cat,$$

where $M^{\neq}$ is the activated complex. The rate of reaction can be formulated as follows:

$$W = k_{eff}c_0 = k_{true}\cdot\frac{a_{\neq}}{f^{\neq}} = k_{true}\, c_X\,\frac{f_X}{f^{\neq}}.$$

Taking into account the equilibrium constant for the formation of X and assuming that X is the Arrhenius complex and that the rate of decomposition of the complex into the catalyst and the substrate is higher than the rate of formation of the reaction product, we obtain

$$c_R = \frac{K_X c_X}{a_{Cat}}\cdot\frac{f_X}{f_R}.$$

Taking into account the material balance equation

$$c_0 = c_R + c_X,$$

we find the general equation for the unimolecular process:

$$k_{eff} = \frac{k_{true}\cdot\dfrac{f_X}{f^{\neq}}}{1+\dfrac{K_X f_X}{a_{Cat}\, f_R}}. \tag{4}$$

If the mechanism of the ionisation of the substrate is known, then, using Hammett's postulate

$$\frac{f_X}{f_R} = \frac{f_{X'}}{f_{In}} = \text{const}$$

we introduce into Eqn. (4) the corresponding acidity or alkalinity. Furthermore, the complex X and the activated complex usually have the same composition, charge, and structure, i.e. $f_X/f^{\neq}$ = const., which greatly simplifies Eqn. (4):

$$k_{eff} = \frac{k_{true}}{1+\dfrac{K_X}{h_X}}. \tag{5}$$

The values of c_X have now been determined by independent methods in a number of studies[48] and the validity of Eqn. (5) has been demonstrated.

B. The Bimolecular Mechanism

In reactions involving a bimolecular mechanism, the activated complex includes the reactant, the catalyst, and, in hydrolytic reactions, a water molecule. In some cases the activated complex is formed when X interacts with a water molecule and in others when the reactant interacts with the complex of the catalyst and a water molecule, for example the hydronium ion.

The rate of reaction can be defined by two identical equations:

$$W = k_{eff}\, c_0 = k_{true}\frac{a_{\neq}}{f^{\neq}} = \begin{cases} k_{true}\,\dfrac{a_R\cdot a_{Cat.H_2O}}{f^{\neq}} \\ k_{true}\,\dfrac{a_{R.Cat.}\cdot a_{H_2O}}{f^{\neq}} \end{cases}.$$

These equations cannot be solved in a general form, since there are as yet no reasonable quantitative methods for estimate $f^{\neq}$. However, there are many empirical approaches. We shall consider briefly some of them, assuming for simplicity that the concentration of R is much higher than of the complex X.

In Bunnett's approach[49], specific hydration numbers are assigned to all the species in the reaction medium. After formulating the equation

$$R\cdot(H_2O)_s + Cat\,(H_2O)_n \overset{K_X}{\rightleftarrows} X\,(H_2O)_p + (s+n-p)\cdot H_2O,$$

$$X\cdot(H_2O)_p + (H_2O)_r \rightleftarrows M^{\neq}\,(H_2O)_t \xrightarrow{k_{true}} \text{products},$$

and taking into account the indicator equilibrium

$$In\,(H_2O)_b + Cat\,(H_2O)_n \rightleftarrows In\cdot Cat\,(H_2O)_c + (b+n-c)\cdot H_2O,$$

we obtain

$$k_{eff} = \frac{k_{true}}{K_X}\cdot h_X\,\frac{f_{R(H_2O)_s}\cdot f_{In\,Cat(H_2O)_c}}{f^{\neq}_{M(H_2O)_t}\cdot f_{In(H_2O)_b}}\cdot a_{H_2O}^{(b-c)-(s-p)+r}. \tag{6}$$

Using Hammett's postulate and assuming that $f_{In\,Cat(H_2O)_c}/f^{\neq}_{M(H_2O)_t}$ is independent of the composition of the medium because the complex of the reactant and the catalyst (or of the indicator and the catalyst) and the activated complex have the same charge and similar structures, we obtain

$$k_{eff} = \frac{k_{true}}{K_X}\cdot h_x\cdot a_{H_2O}^r. \tag{7}$$

Bunnett treated in terms of this equation numerous data for the hydrolysis of various compounds[49]. However, Eqn. (7) is frequently inapplicable when the catalyst concentration range is fairly wide. Strictly speaking, one cannot assume that the ratio $f_{\mathrm{In\,Cat(H_2O)_c}}/f^{\neq}_{\mathrm{M(H_2O)_t}}$ is constant in Eqn. (6), because the two complexes should have different compositions (differ hydration numbers); however, the lack of knowledge of this ratio is compensated by an empirical parameter r, formally expressing the number of water molecules involved in the activated complex.

Vinnik's approach[50] consists in the hypothesis that an intermediate complex M (of R and H_3O^+) is formed in aqueous solutions of strong acids and decomposes unimolecularly into the reaction products. It is assumed that the activity coefficient ratio $f_M/f^{\neq}$ is constant and the activity coefficients of the activated complex and the complex M are given by the equation

$$f_M = f^{\neq} = f_R^{\beta}\, f^{\alpha}_{H_3O^+}\ \mathrm{const},$$

where α and β are parameters independent of the medium,

$$k_{\mathrm{eff}} = \frac{k_{\mathrm{true}}}{K_X}\cdot c_{H_2O} + f_R^{(1-\beta)}\ f^{(1-\alpha)}_{H_3O^+},$$

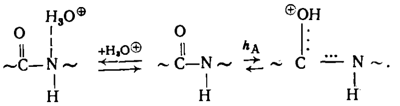
and f_R can be determined from solubility data. Thus the problem reduced to the determination of the parameters α and β alone.

In recent years Vinnik[51] formulated a general rule for the determination of the mechanism of the rate-limiting step in catalytic hydrolysis in aqueous solutions: the activity of the activated complex must be expressed in terms of the concentrations of different forms of the reactants in such a way that the multiplier involving the activity coefficients which appears in the kinetic equation does not vary with the concentration of the acid. Using extensive experimental data, Vinnik divided all the hydrolytic reactions in aqueous solutions of strong acids into four groups. In reactions of groups I and II, the activated complex is produced from the unionised form of the reactant, the hydronium ion, and the nucleophilic agent—water molecule (group I) or anion (group II). In the reactions of the other groups, the activated complex is produced from the protonated form of the reactant with or without the participation of a water molecule (group III) or with participation of the anion (group IV).

Thus, whereas a simple general equation, obtained within the framework of reasonable assumptions is available for unimolecular processes, such an equation does not exist for bimolecular processes and in each specific case additional information is necessary for the choice of the mechanism.

We shall consider the mechanisms of the decomposition of chemically unstable bonds in polymers.

The amide linkage. A characteristic feature of the hydrolytic reactions of compounds with an amide linkage in acid media is a maximum in the effective rate constant as a function of the concentration of the acid. Fig. 4 illustrates the variation of $\lg k_{\mathrm{eff},25°}$ for the hydrolysis of the cyclic caproamide trimer (a polymer model) as a function of the amide acidity function of aqueous solutions of sulphuric acid H_A.[15,52] The values of $\lg k_{\mathrm{eff},25°}$ for the hydrolysis of the polymer with M_V = 20 000 lie almost on the same curve. According to the proposed mechanism, the rate-limiting step of the process is the attack by the hydronium ion on the amide nitrogen atom; the protonation of the carbonyl oxygen leads to the formation of the unreactive form:



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H_3O^{\oplus}}{\vdots}}{N}}\sim \ \underset{\longrightarrow}{\overset{+H_3O^{\oplus}}{\longleftarrow}}\ \sim\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}\sim \ \overset{h_A}{\rightleftarrows}\ \sim\overset{\overset{\displaystyle {}^{\oplus}OH}{\vdots}}{C}\ \overset{\cdots}{-}\ \underset{\underset{\displaystyle H}{|}}{N}\sim.$$

The variation of k_{eff} with thermodynamic parameter is described satisfactorily by the equation

$$k_{\mathrm{eff}} = \frac{k_{\mathrm{true}}\ c_{H_3O^+}}{1+\dfrac{h_A}{K_{BH^+}}}. \tag{8}$$

The continuous line in Fig. 4 was calculated theoretically from this equation.

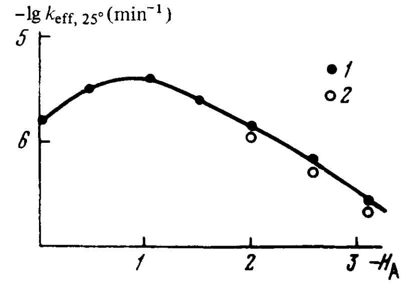


Figure 4. Variation of $\lg k_{\mathrm{eff},25°}$ for the hydrolysis of the cyclic caproamide trimer (1) and polycaproamide having $\overline{M}_V$ = 20 000 (2) with the amide acidity function of aqueous sulphuric acid solutions[15].

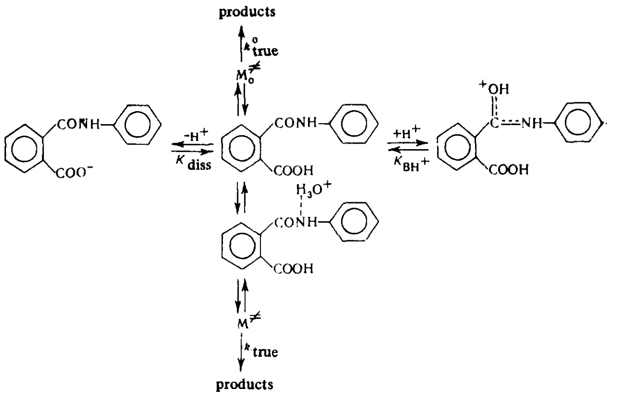
Thus the hydrolysis of compounds with an amide bond is described by the A-2 mechanism. Attention should be drawn to two facts of practical importance:

1. The hydrolytic stability of compounds with an amide linkage increases greatly in concentrated solutions of acids.
2. In polycaproamide the amide linkages are kinetically independent, since the five methylene groups completely prevent the transmission of the mutual polar influence of the amide linkages.

The study of the hydrolysis of o-substituted aromatic amides, simulating the non-cyclised units in heterocyclochain polymers, is of considerable interest. The presence of o-substituents is responsible for a number of characteristic features of the acid hydrolysis of these amides, namely the hydrolytic reaction may be accompanied by the cyclisation reaction and in dilute acid solutions intramolecular catalysis may occur.

Fig. 5 illustrates the variation of $\lg k_{\mathrm{eff},25°}$ with H_A for the hydrolysis and cyclisation of 2-benzamidophenol and the hydrolysis of 2-phenylbenzoxazole—the model compounds for polybenzoxazole[53]. Kinetic analysis of the results showed that the variation of k_{eff} is described by Eqn. (8) for all three reactions.

Fig. 6 presents kinetic data for the acid hydrolysis of N-phenylphthalamic acid—the model of aromatic polyamidoacids[54]. In order to interpret the experimental data, a mechanism was adopted according to which unreactive forms are produced on protonation of the carbonyl oxygen of the amide linkage and on dissociation of the carboxy-group. The reactive species is the unionised form, which may react either with the carboxy-group (intramolecular catalysis) or with a hydronium ion (specific acid catalysis).



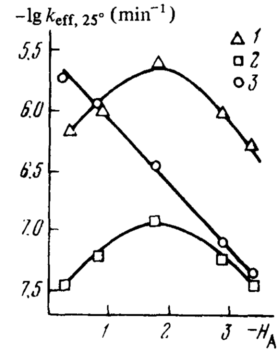


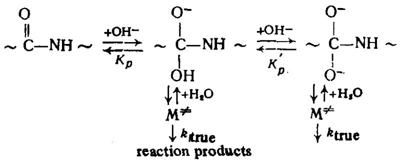
Figure 5. Variation of $\lg k_{eff}$ with the amide acidity function of aqueous sulphuric acid solution for the hydrolysis (1) and cyclisation (2) of 2-benzamidophenol and the hydrolysis of 2-phenylbenzoxazole (3).[53]

The general expression for k_{eff} is

$$k_{eff}=\frac{k_{true}\,c_{H_3O^+}+k^0_{true}}{1+\frac{K_{diss}}{h_A}+\frac{h_A}{K_{BH^+}}},$$

where k_{true} and $\overset{0}{k}_{true}$ are the true rate constants for hydrolysis via the specific acid and intramolecular catalytic mechanisms and K_{diss} is the dissociation constant of N-phenylphthalamic acid.

In alkaline media there is also a complex profile of changes in the alkaline hydrolysis of compounds with amide linkages. Fig. 7 illustrates the variation of $\lg k_{eff,25°}$ for the hydrolysis of N-methylacetamide with the alkalinity function of aqueous KOH solutions[55]. It has been shown by infrared spectroscopy that amides may exist both in the unionised form and as singly and doubly charged ions. The rate-limiting step in the process involves the interaction of these ions with a water molecule:



$$\sim\overset{O}{\overset{\|}{C}}-NH\sim \underset{K_p}{\overset{+OH^-}{\rightleftarrows}} \sim\underset{OH}{\overset{O^-}{C}}-NH\sim \underset{K'_p}{\overset{+OH^-}{\rightleftarrows}} \sim\underset{O^-}{\overset{O^-}{C}}-NH\sim .$$

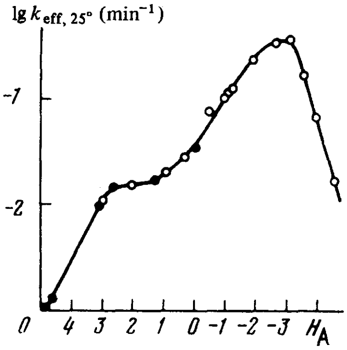


Figure 6. Variation of $\lg k_{eff,25°}$ with the amide acidity function of aqueous sulphuric acid solutions for the hydrolysis of N-phenylphthalamic acid[54].

The kinetic equation for the hydrolysis is

$$k_{eff}=\frac{k_{truc}\,a^2_{H_2O}\,K_p\cdot\frac{1}{b_0}+k'_{true}a_{H_2O}}{1+K'_p\frac{a_{H_2O}}{b_0}+K_pK'_p\frac{a_{H_2O}}{b_0^2}}, \qquad (9)$$

where b_0 is the alkalinity of the medium.

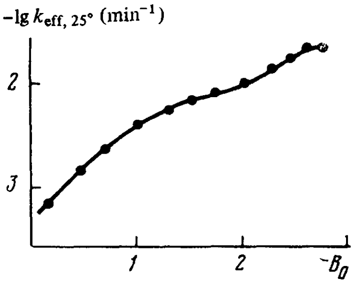


Figure 7. Variation of $\lg k_{eff,25°}$ with the alkalinity function of aqueous potassium hydroxide solutions for the hydrolysis of N-methylacetamide[55].

The validity of this equation has been demonstrated by an independent procedure involving a comparison of the changes in k_{eff} with the concentrations of the ionised forms of the amide[56].

The ester linkage. Numerous studies have been made on the acid hydrolysis of compounds with ester linkages, but there is as yet no unanimous view concerning the mechanism of the hydrolysis. The possible mechanisms of the hydrolytic reactions have been analysed in detail[51]. The hydrolysis of compounds with ester linkages in alkaline media proceeds via a mechanism[51] analogous to that described above for compounds with amide linkages.

The imide linkage. The hydrolysis of compounds with imide linkages takes place in acid and alkaline media via mechanisms analogous to those described for amides.

The acetal linkage. Compounds with acetal linkages are known to be stable in alkalis and to be readily hydrolysed in acids. The acid-catalysed hydrolysis of acetals is an example of the A-1 monomolecular mechanism[58,59]. The experimental data are described by the equation

$$k_{\text{eff}} = \frac{k_{\text{true}}}{K_{\text{BH}^+}} \cdot h_0,$$

where h_0 is the Hammett acidity function.

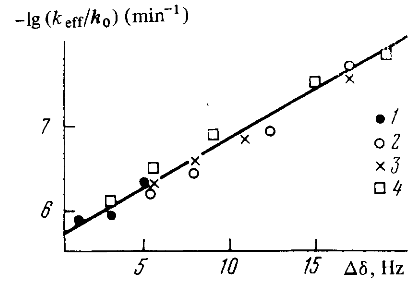
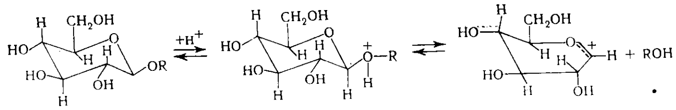


Figure 8. Experimental data represented by a plot of $\lg(k_{\text{eff}}/k_0)$ against $\Delta\delta$ for the hydrolysis of cellobiose in aqueous acid solutions: 1) HCl; 2) $HClO_4$; 3) H_2SO_4; 4) H_3PO_4.[61]

In the hydrolysis of cyclic hemiacetals (glycosides) the principle of correspondence between the structure of the protonated species and the activated complex does not hold. For example, the rate-limiting stage in the hydrolysis of cellobiose, a model of cellulose, includes a slow transition from the chair conformation (protonated form) to the half-chair conformation in the activated complex[60]:



The ratio $f_X/f^{\neq}$ in Eqn. (4) cannot then be regarded as constant. Evidently it will be larger the stronger the interaction between the cellobiose molecule and the medium.

The change in the activity coefficient ratio $f_{RH^+}/f^{\neq}$ can be estimated from the chemical shifts $\Delta\delta$ of the protons at the carbon atom in the 2-position[61]. The change in k_{eff} for the hydrolysis of cellobiose is described by the equation

$$\lg \frac{k_{\text{eff}}}{h_0} = \lg \frac{k_{\text{true}}}{K_{\text{BH}^+}} + p \cdot \Delta\delta,$$

where p is a proportionality coefficient. Fig. 8 presents experimental data in terms of the variables of this equation for aqueous solutions of different acids.

For the other linkages encountered in polymers, the evidence adduced for the hydrolytic mechanisms is not rigorous.

IV. PRINCIPAL TYPES OF DECOMPOSITION OF POLYMERIC MOLECULES

The structure of polymeric molecules determines the type of their decomposition. On the one hand, chemically unstable bonds can be equally reactive and, on the other, terminal bonds can exhibit enhanced reactivity, which complicates the chemical degradation process. Furthermore, polymers may contain bonds with enhanced reactivity—"weak bonds".

The kinetics (changes in the number of molecules and in the mass of the polymer) have been examined theoretically[62] for the principal types of decomposition of polymeric molecules in degradation processes. We shall consider the main types of decomposition of polymeric molecules in chemical degradation reactions.

a. Random Decomposition

This type of decomposition is frequently encountered in chemical degradation processes and can be illustrated by the examples in Tables 2 both for the reactions of the main polymer chain and for the polymer-analogue reactions involving the abstraction of groups of atoms without a change in the degree of polymerisation.

In cellulose the terminal hemiacetal linkages are somewhat more reactive than the "non-terminal" linkages. This is seen from a comparison of the rate constants for the acid-catalysed hydrolysis of cellulose and cellobiose (Table 2) and also from data[63] showing that the reactivities of the two hemiacetal linkages in cellotriose differ by 1.5. However, the difference between the reactivities of the terminal and non-terminal linkages is slight and the acid-catalysed hydrolysis of cellulose under homogeneous conditions can therefore be regarded as a random process to a first approximation.

b. Depolymerisation Decomposition

This type of decomposition is encountered extremely rarely in a pure form in chemical degradation processes; it is usually combined with the random decomposition of the polymer chain.

c. Decomposition of the Mixed Type

A typical example of such decomposition is the acid-catalysed degradation of polyoxymethylene, which is accompanied by the cleavage of the chain with formation of fragments having terminal hydroxy-groups and by the depolymerisation of these fragments.

d. The Cleavage of the Polymer Chain

The maximum in the reactivity of polyoxymethylene oligomers with terminal methoxy-groups (POM-OCH_3) in the acid-catalysed degradation process (Table 6) leads to the conclusion[64] that the terminal acetal linkages are more reactive than the non-terminal linkages and that the acid-catalysed degradation process includes two consecutive stages: (1) slow decomposition of the terminal acetal linkage in the oligomer; (2) rapid depolymerisation of the hemiacetal formed.

Table 6. Aliphatic reaction constants σ^* and the rate constants for the degradation of the $CH_3(OCH_2)_nOCH_3$ oligomers in aqueous sulphuric acid solutions[64].

n	R_1^a	R^a	$\Sigma\sigma^*$	$\lg K^b_{25°}$	n	R_1^a	R^a	$\Sigma\sigma^*$	$\lg K^b_{25°}$
1	CH_3	CH_3	0	−2.82	3	»	$(CH_2O)_2CH_3$	0.15	−2.64
2	»	CH_2OCH_3	0.52	−2.18	4	»	$(CH_2O)_3CH_3$	0.05	−2.74

[a] Substituents near the reaction centre.
[b] $k_{25°} = (k_{true}/K_{BH^+})_{25°}$, where k_{true} is the true rate constant for the decomposition of the protonated form of the reactant and K_{BH^+} is the basicity constant of the reactant.

The results are described satisfactorily by the Taft equation (Fig. 9) and make it possible to select methylal ($n = 1$) as a model of the terminal acetal linkage in POM-OCH_3 polymers.

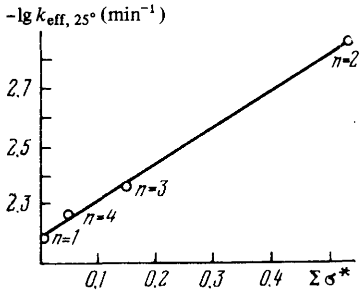


Figure 9. Correlation based on the Taft equation of the experimental data for the degradation of polyoxymethylene oligomers with terminal methoxy-groups in aqueous sulphuric acid solutions[64].

The reactivities of certain acetal linkages have been determined[65] from the change in the molecular weight of POM-OCH_3 in the course of degradation in a water–hexafluoroacetone solution of HCl. Table 7 shows that the terminal acetal linkages are approximately five times more reactive than the "non-terminal" linkages.

e. The Depolymerisation Reaction

This reaction occurs when the polyoxymethylene molecule contains terminal hydroxy-groups (POM-OH), which serve as active centres for the depolymerisation reaction.

Table 7. The rate constants for the decomposition of terminal and non-terminal acetal linkages and for depolymerisation in the acid-catalysed degradation of POM-OCH_3 in water–hexafluoroacetone solutions of HCl at 25°C.

	k, litre mole^{-1} min^{-1}		
water concn., M	decomposition of terminal bonds	decomposition of non-terminal bonds (random process)	depolymerisation
8.99	$(1.1\pm0.2)\cdot10$	2 ± 0.4	$(3\pm1)\cdot10$
55.5	$(3.1\pm0.2)\cdot10^{-3}$	—	6 ± 1

In stepwise depolymerisation of polymers with an exponential molecular weight distribution, the molecular weight remains almost constant, i.e. $(dM_n/dt)_{dep} \simeq 0$. When the decomposition of the polymeric molecules is a random process followed by depolymerisation (the length of the kinetic depolymerisation chain is much smaller than the number-average degree of polymerisation), we therefore obtain the following system of equations:

$$\frac{dm}{dt} = -2k_{rand}N - 2k_{dep}N; \tag{10}$$

$$\frac{dN}{dt} = k_{rand}m - 3k_{rand}N - \frac{2k_{dep}N^2}{m}, \tag{11}$$

where m and N are respectively the mass of the polymer and the number of molecules at time t, k_{rand} and k_{dep} are respectively the rate constants for random and depolymerisation decomposition. For the initial conditions $m = m_0$ and $N = 0$ with $t = 0$, Eqns. (10) and (11) have the following solution:

$$m = m_0 \exp\left\{\left(\frac{2k_{rand}}{k_{rand}} + 1\right)[\ln(2 - \exp - k_{rand}t) - k_{rand}t]\right\},$$

from which it is possible to calculate the depolymerisation rate constant (Table 7).

This relation between the rate constants for the decomposition of the terminal and non-terminal acetal linkages and for depolymerisation is responsible for the virtually identical effective rate constants determined from the accumulation of formaldehyde in the degradation of POM with different terminal groups in water–hexafluoroacetone solutions of HCl (Table 8). Thus the acid-catalysed degradation of POM in water–hexafluoroacetone solutions takes place in a complex manner; during the initial period, the random dissociations and the decomposition of the terminal acetal linkages lead to the formation of a considerable number of POM-OH molecules, which depolymerise with liberation of formaldehyde, the amount of POM-OH being almost independent of the molecular weight of the initial polymer and the nature of its terminal group.

It is noteworthy that the random decomposition and depolymerisation reactions have different mechanisms. The acetal linkage is decomposed via the A-1 mechanism[59,66], while the depolymerisation reaction proceeds via the A-2 mechanism[67]. Thus the relation between the rate constants for these reactions changes when there is an appreciable alteration of the acid concentration. An equation describing the variation of the effective rate constants for the degradation of POM-OH, determined from the accumulation of formaldehyde, in aqueous sulphuric acid solutions (5–50 wt.%) has been derived[67]:

$$k_{\text{eff}} = k_{\text{dep(true)}}\, c_{\text{H}_3\text{O}^+} \left(\frac{1}{M_{n_0}} + \frac{k_{\text{rand(true)}}\, h_0}{K_{\text{BH}^+}\, k_{\text{term(true)}}\, c_{\text{H}_3\text{O}^+}} \right),$$

where $k_{\text{dep(true)}}$ is the true depolymerisation rate constant and $k_{\text{term(true)}}$ the true rate constant for the destruction of active depolymerisation centres in consequence of the degradation of the polymer chain. When

$$\frac{k_{\text{dep(true)}}}{\overline{M}_{n_0}} \gg \frac{k_{\text{dep(true)}} k_{\text{rand(true)}}}{K_{\text{BH}^+}\, k_{\text{term(true)}}} \cdot \frac{h_0}{c_{\text{H}_3\text{O}^+}}$$

only the depolymerisation reaction takes place and is determined by the initial concentration of the OH terminal groups in POM-OH. This condition holds in dilute sulphuric acid solutions (<5 wt.%) for POM-OH ($\overline{M}_V$ = 7000). With increase of the acid concentration, the depolymerisation reaction, determined by the terminal groups formed on random cleavage of the polymer chain, begins to play a major role and when

$$\frac{k_{\text{dep(true)}}}{\overline{M}_{n_0}} \ll \frac{k_{\text{dep(true)}} k_{\text{rand(true)}}}{K_{\text{BH}^+}\, k_{\text{term(true)}}} \cdot \frac{h_0}{c_{\text{H}_3\text{O}^+}}$$

we obtain

$$k_{\text{eff}} = \frac{k_{\text{rand(true)}} k_{\text{dep(true)}}}{K_{\text{BH}^+}\, k_{\text{term(true)}}} \cdot h_0,$$

i.e. the acid-catalysed degradation process obeys the *A*-1 mechanism.

Table 8. The effective rate constants for the degradation of POM having different molecular weights and different terminal groups in 4.4 × 10^{-3} M HCl solution (8.99 M H_2O in hexafluoroacetone at 30°C [65]).

Polymer	$\overline{M}_V$	$10^2 k_{\text{eff}}$, min^{-1}	Polymer	$\overline{M}_V$	$10^2 k_{\text{eff}}$, min^{-1}
POM-OCH_3	1 500	3.8	POM-$OOCCH_3$	50 000	3.4
	6 500	3.6		100 000	3.4
	10 500	3.7	POM-OH	7 000	19*
	19 500	3.9		220 000	3.5

*Initially there is a large number of depolymerisation centres.

The type of decomposition of the molecules in the solid polymer may differ from that in solution. For example, according to one of the models, cellulose molecules have a folded conformation in the protofibrils and in each fold there are about eight elementary units[68]. On the basis of this structure, Manley and coworkers[69] suggested that the hemiacetal linkage at the tops of the folds exhibit an enhanced reactivity. To confirm this, experiments were performed on the acid-catalysed degradation of different types of cellulose under heterogeneous conditions and molecular weight distribution (MWD) curves were obtained for the acid-soluble degradation products and for the insoluble residue at different time intervals up to 70% conversion. In the course of the degradation process, the cellulose molecules broke down into fragments with an average degree of polymerisation of about 8 regardless of the type of polymer and the MWD of the unreacted component of the cellulose did not change. The results confirm the hypothesis of the presence in cellulose of at least two types of linkage differing appreciably in their reactivities; hemiacetal linkages at the tops of the folds are more reactive than the hemiacetal linkages in the remaining portions of the folds.

Thus in the decomposition of polymers in corrosive media there is a possibility in the general case of sets of bonds having different reactivities. This in fact determines the type of decomposition of polymeric molecules.

V. DIFFUSION OF CORROSIVE MEDIA INTO POLYMERIC MATERIALS

In order to determine the mechanism of the degradation of polymeric materials in corrosive media, it is necessary to know how the corrosive medium diffuses into the polymer and what is its state within the polymer, i.e. to what extent the electrolyte is dissociated into ions and how much the latter are solvated by the solvent.

Since the diffusion of corrosive media into polymers is of considerable theoretical and practical interest (for example in connection with the prediction of the protective properties of polymeric coatings, the permeability of biological membranes, etc.), it will be necessary to consider in this section the general characteristics of the diffusion of corrosive media into polymeric materials. There is at present no general quantitative theory relating the diffusion coefficients of electrolytes in polymers to any structural parameters of the latter. Polymers are usually divided into two classes: hydrophilic and hydrophobic; the principal characteristics of the diffusion of electrolyte solutions into such polymers have been described in a number of studies[70–72].

It is useful to examine the diffusion of electrolytes into polymers as a function of their content of the solvent, for example water. Polymers can be divided arbitrarily into three groups:

(a) polymers readily dissolving water (50–80 wt.%);

(b) polymers dissolving water to a limited extent (1–50 wt.%);

(c) polymers dissolving water sparingly (<1 wt.%).

One should bear in mind that polymers in groups (a) and (b) are as a rule hydrophilic and those in group (c) are hydrophobic.

Polymers of Group (a)

A typical polymer of this group is poly(vinyl alcohol); the solubility of water in this polymer lies in the range 60–80% depending on the method of synthesis. The influence of the polymer on the diffusing species is slight and largely reduces to the bending of the polymer molecules by the diffusing substance. The Mackie–Meares theory[73], which takes into account such bending, makes it possible to calculate the diffusion coefficients fairly rigorously. As a rule electrolytes dissociate into ions in such polymers to the same extent as in aqueous solutions[74]. If the electrolyte in the polymer matrix is not completely dissociated, then in the general case the effective diffusion coefficient depends on the electrolyte concentration. This effect is associated with the different mobilities of ions and undissociated molecules in the polymer matrix[74].

its time variation is described by one of the adsorption equations.

(c) The attainment of a steady concentration of the diffusing substances on the surface of the polymeric article is determined by certain mass-transfer laws, the simplest of which is

$$j = \beta (c_S - c_V),$$

where j is the flux of the diffusing substance, c_S and c_V are respectively the concentration of the substance on the surface and in the bulk of the corrosive solution, and β is the mass-transfer coefficient.

Solution of the Equations for Polymeric Articles of Different Shapes

Most of the practical problems reduce to the description of degradation processes in bodies of simple shape. Polymeric films and coatings are modelled by layers of infinite extent, fibres are modelled by a cylinder, etc. The solutions of Eqns.(12)–(14) for a layer of infinite extent will be considered below. Depending on the ratio of the rates of diffusion and chemical reaction, chemical degradation can proceed under different conditions:

(a) the rate of diffusion of the corrosive medium is comparable to the rate of the chemical reaction (the degradation process takes place in a reaction zone whose size increases with time, and reaches in the limit the dimensions of the polymeric article), i.e. the reaction takes place in the internal diffusion-kinetic region.

(b) The rate of diffusion of the corrosive medium greatly exceeds the rate of the chemical reaction. After the entire polymer has swollen in the corrosive medium, the degradation process takes place throughout the bulk of the polymer, i.e. in the internal kinetic region.

(c) The rate of diffusion of the corrosive medium is much lower than the rate of the chemical reaction. In this case the degradation process takes place in a thin surface reaction layer, which is usually described as reaction from the surface of the article, i.e. in the external diffusion-kinetic region.

b. Internal Diffusion-kinetic Region

The simultaneous solution of Eqns.(12)–(14) constitutes a difficult mathematical problem, which can only be solved with the aid of a computer.

Consideration of the diffusion of the corrosive medium in polymers showed that the diffusion of the solvent is frequently much faster than the direct diffusion of the catalyst (acid or base), i.e. $D_{\text{solv}} > D_{\text{cat}}$; one can therefore assume that the concentration of the solvent in the reaction zone of the polymeric article is constant and equal to its solubility in the polymer (c^0_{solv}), i.e.

$$c_{\text{solv}} = c^0_{\text{solv}} \,. \tag{17}$$

Thus the problem simplifies and reduces to the solution of Eqns.(12) and (13), the first of which assumes the following form when account is taken of Eqn.(17):

$$\frac{dc_n}{dt} = kc^0_n c^0_{\text{solv}}\, c_{\text{Cat}} = k_{\text{eff}} \cdot c_{\text{Cat}}, \tag{18}$$

where

$$k_{\text{eff}} = k\, c^0_n\, c^0_{\text{solv}}.$$

For simplicity, we shall confine ourselves to only one term in Eqn.(13) and shall put $c_i = c_n$.

Consider the case where $K_p \to \infty$, i.e. the functional groups formed during degradation react almost completely with the catalyst. When account is taken of the fact that this reaction proceeds much faster than the degradation reaction, Eqn.(13) becomes

$$\frac{\partial c_{\text{Cat}}}{\partial t} = D_{\text{Cat}} \frac{\partial^2 c_{\text{Cat}}}{\partial x^2} - k_{\text{eff}}\, c_{\text{Cat}}\,, \tag{19}$$

where x is the diffusion coordinate.

The solution of Eqn.(19) subject to the boundary conditions $c_{\text{cat}} = c^0_{\text{cat}}$ when $x = 0$ and l and the initial condition $c_{\text{cat}} = 0$ when $t = 0$ and $0 \leqslant x \leqslant l$ is the following:

$$c_{\text{Cat}}(x, t) = c^0_{\text{Cat}}\left\{1 - \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\sin b_m x}{(2m-1)(b^2_m D_{\text{Cat}} + 1)} \times \right.$$
$$\left. \times [k_{\text{eff}} + b^2 m D_{\text{Cat}} \exp - (b^2_m D_{\text{Cat}} + k_{\text{eff}})\, t]\right\}, \tag{20}$$

where $b_m = \pi(2m-1)/l$, c^0_{cat} is the solubility of the catalyst in the polymer, and l is the thickness of the film.

After substituting Eqn.(20) in Eqn.(18) and after double integration from 0 to t and from 0 to $l/2$, we obtain

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}} t \left\{1 - \frac{8}{\pi l} \sum_{m=1}^{\infty} \frac{k_{\text{eff}} t\, (b^2_m D_{\text{Cat}} + k_{\text{eff}}) + b^2_m D_{\text{Cat}} [1 - \exp - (b^2_m D_{\text{Cat}} + k_{\text{eff}})\, t]}{(2m-1)\, b_m (b^2_m D_{\text{Cat}} + k_{\text{eff}})^2\, t}\right\}. \tag{21}$$

Analysis of Eqn.(21) makes it possible to distinguish two cases:

(a) $b^2_m D_{\text{cat}} > k_{\text{eff}}$. In this case it is sufficient to retain only the first term of the series. A detailed solution in this instance will be described below.

(b) $b^2_m D_{\text{cat}} < k_{\text{eff}}$. Restriction to only the first term of the series is not permissible and one must bear in mind that, for fairly large values of t,

$$c_n = k_{\text{eff}} c^0_{\text{Cat}}\, t. \tag{22}$$

This case will also be analysed below.

When $K_p \to 0$, i.e. the functional groups formed during the reaction do not interact with the catalyst, Eqn.(19) becomes

$$\frac{\partial c_{\text{Cat}}}{\partial t} = D_{\text{Cat}} \cdot \frac{\partial^2 c_{\text{Cat}}}{\partial x^2}.$$

It solution, subject to analogous boundary and initial conditions, is

$$c_{\text{Cat}}(x, t) = c^0_{\text{Cat}}\left(1 - \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\sin b_m x}{2m-1} \exp - b^2_m D_{\text{Cat}}\, t\right). \tag{23}$$

After substituting Eqn.(23) in Eqn.(18) and after integrating between the same limits as for Eqn.(21), we obtain

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}}\, t \left\{1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} [1 - \exp - (2m-1)^2 y] \frac{1}{(2m-1)^4 y}\right\}, \tag{24}$$

where

$$y = \frac{\pi^2 D_{\text{Cat}}\, t}{l^2}.$$

When $y < 1$, this case obtains during the initial period of the degradation reaction for films of any thickness:

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}}\, t\, \frac{8}{\pi^2} \varphi(y), \tag{25}$$

where

$$\varphi(y) = \sum_{m=1}^{\infty} \frac{\exp - (2m-1)^2 y - 1 + (2m-1)^2 y}{(2m-1)^4 y}.$$

Polymers of Group (b)

These include, for example, polycaproamide, epoxy-resin, and ethylcellulose. The solubility of water in these polymers at 25°C is about 7–9 wt.% for the first two and 2 wt.% for the last[12].

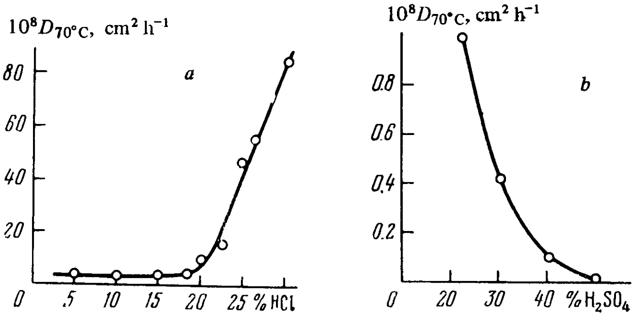


Figure 10. Variation of the diffusion coefficients of hydrochloric (*a*) and sulphuric (*b*) acids in epoxy-resin as a function of acid concentration[72].

Differences are observed in the behaviour in these polymers of electrolytes having high and low vapour pressures. Fig. 10 illustrates the variation of the diffusion coefficients of hydrochloric and sulphuric acids in epoxy-resin at 70°C as a function of the acid concentration[72].

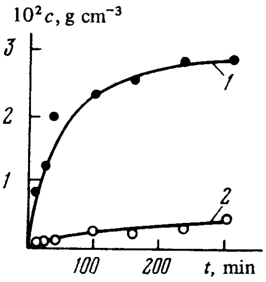


Figure 11. Variation of the concentration of water (1) and HCl (2) during the diffusion of the vapour of 28% hydrochloric acid into an ethylcellulose film at 35°C.[76]

Shterenzon et al.[75] believe that hydrogen chloride can exist in two-forms in polyethylene: in the non-hydrated form and as hydrates, the diffusion coefficient of the former being much higher. With decrease of the water content, there is a change in the ratio of the hydrated and non-hydrated forms of hydrogen chloride, which leads to an increase of the effective diffusion coefficient and in concentrated hydrochloric acid solutions the latter approaches that of gaseous hydrogen chloride.

In sulphuric acid solutions, diffusion coefficient and the water content in the polymer vary in parallel. In contrast to polymers of group (a), the polymers considered here sorb selectively the electrolyte and water.

Fig. 11 illustrates the variation of the concentration of water and HCl during the diffusion of the vapour of 28% hydrochloric acid solution into an ethylcellulose film at 35°C. The diffusion of the components of the corrosive medium proceeds with similar diffusion coefficients, but the ratio of the concentrations of water and HCl in the polymer is approximately ten times greater than in the gas phase[76].

Electrolytes are dissociated into ions in polymers of this kind, but quantitative data on the degree of dissociation are not available.

Polymers of Group (c)

This group includes the majority of industrially important polymers. Electrolytes with a high vapour pressure diffuse with diffusion coefficients close to those for polymers of groups (a) and (b). Electrolytes with a low vapour pressure diffuse into these polymers at very low rates[77].

VI. THE INFLUENCE OF THE SOLID STATE OF THE POLYMER ON THE DEGRADATION PROCESS

The degradation reactions in solid polymers have a number of characteristics which are associated both with the specific features of the structures of polymeric materials and with the specific features of the kinetics of heterogeneous reactions. We shall consider the characteristics of the structures of polymeric materials.

1. THE INHOMOGENEITY OF THE STRUCTURES AND PROPERTIES OF POLYMERS

The structural characteristics and properties of polymeric materials are almost always anisotropic with respect to volume, which is frequently referred to as spatial gradients[78]. For single-phase systems, the following examples of structural gradients may be quoted:

(a) vitreous and viscoelastic sections (copolymers of methyl methacrylate and methyl acrylate);

(b) strongly and weakly cross-linked regions (vulcanised elastomers);

(c) oriented and non-oriented regions (crystallising polymers);

(d) regions with different MWD (fractionated during shear flow);

(e) regions with different degrees of order in single-phase amorphous polymers (association).

The following structural gradients are characteristic of heterophase systems:

(a) amorphous and crystalline regions (crystalline polymers);

(b) regions with different degrees of microheterogeneity (stereoregular polymers);

(c) regions with different steric (*cis–trans* groups) or chemical structures (statistical copolymers).

In real polymeric materials there are in addition a wide variety of structural gradients established by added organic and inorganic substances: stabilisers, plasticisers, pore-forming agents, fillers (fibreglass in laminated glass plastics and carbon black in rubbers), dyes, etc.

The above structural gradients are responsible for the anisotropy of the chemical and diffusion properties of polymeric materials. At present there are no rigorous quantitative data concerning the influence of structural factors on the diffusion of corrosive media, on the one hand, and on the reactivity of the functional groups in polymeric materials, on the other. Isolated data on these problems have been published[79,80].

2. KINETICS OF THE DEGRADATION OF POLYMERS

The degradation of polymers in liquid corrosive media proceeds via the following principal stages:

(1) adsorption of the corrosive medium on the surface of the polymeric article;

(2) diffusion of the corrosive medium into the bulk of the polymeric article;

(3) chemical reaction of the corrosive medium with the chemically unstable bonds of the polymer;

(4) diffusion of the degradation products to the surface of the polymeric article;

(5) desorption of the degradation products from the surface of the polymeric article.

Examination of all the stages of the degradation process is difficult, because it is usually assumed that one or at most two stages are slow compared with the others, and therefore limit the rate of the entire degradation process. Stages (1) and (5) are usually faster than stages (2)–(4). The diffusion of the degradation products to the surface of the polymeric articles does not usually play a significant role in the estimation of the changes in the useful properties of the polymer during the degradation of polymeric articles, but it may limit, for example, the rate of biological degradation of the polymer in a living organism.

a. Fundamental Equations

In the general case (assuming that the law of mass action holds), the rate of decomposition of chemically unstable bonds in a polymer under the influence of a corrosive medium is

$$W = \frac{dc_n}{dt} = k(c_n^0 - c_n)\, c_{\text{Cat}}\, c_{\text{solv}}, \qquad (12)$$

where c_n^0 is the initial concentration of the chemically unstable bonds in the polymer, c_n the concentration of the dissociated bonds, c_{cat} the concentration of the catalyst in the polymer, and c_{solv} the concentration of the solvent in the polymer.

The concentration of the catalyst (for example an acid or a base) in the polymer can be found from Fick's equation:

$$\frac{\partial c_{\text{Cat}}}{\partial t} = D_{\text{Cat}} \nabla^2 c_{\text{Cat}} - \sum_i^0 c_{\text{Cat}}\, c_i\, K_{p_i}, \qquad (13)$$

where ∇^2 is the Laplace operator, c_i the concentration of the functional groups in the polymer capable of involvement in complex-formation or substitution reactions, and K_{p_i} are the equilibrium constants for the complex-formation or substitution reactions. The second term on the right-hand side of Eqn.(13) takes into account the possibility of reactions such as protonation, the conversion of carboxy-groups, etc.

If the solvent is consumed in the steps involving the decomposition of the chemically unstable bonds in the polymer (for example, water is consumed in hydrolytic reactions), then the concentration of the solvent can be found from the equation

$$\frac{\partial c_{\text{solv}}}{\partial t} = D_{\text{solv}} \nabla^2 c_{\text{solv}} - k(c_{n^0} - c_n)\, c_{\text{Cat}}\, c_{\text{solv}}. \qquad (14)$$

In order to formulate these equations, a number of assumptions must be justified:

(a) the polymer–corrosive medium system is as a rule extremely dilute with respect to the corrosive medium, i.e. one may assume that D_{cat} and D_{solv} are independent of the concentrations of the corresponding components in the polymer. When the corrosive medium is very soluble in the polymer, it is necessary to use the equation taking into account the relation between D and the concentration of the diffusant.

(b) k is constant. This is true for low solubilities of the corrosive medium in the polymer. In general, the influence of the corrosive medium on k can be reduced, to a first approximation, to the influence of the solvent on the rate of the chemical reaction and may be predicted on the basis of the existing theories[10].

(c) The decomposition of the chemically unstable bonds is almost irreversible. This condition holds for the degradation process in a thin surface layer, or in a reaction zone up to low degrees of conversion (<0.02). The concentration of the chemically unstable bonds then remains almost constant and $c_n^0 - c_n \simeq c_n^0$.

(d) The properties of the polymer are homogeneous with respect to volume. In reality there are regions in the polymer where the reactivity may be different (different values of k) and which exhibit a different capacity to sorb corrosive media and allow them to diffuse (different c_0 and D). The rigorous expression for the overall rate of the degradation process should therefore assume the following form:

$$W_\Sigma = \sum_i [k(c_n^0 - c_n)\, c_{\text{Cat}}\, c_{\text{solv}}]_i\, V_i, \qquad (15)$$

where V_i is the relative volume of each region. The use of Eqn.(14) involves considerable difficulties, so that in most cases one has to employ the concept of the average rate. We shall define it as the ratio of the overall rate of the process to the total volume of the polymeric article:

$$\overline{W} = \frac{\sum_i [k(c_n^0 - c_n)\, c_{\text{Cat}}\, c_{\text{solv}}]_i\, V_i}{\sum_i V_i}. \qquad (16)$$

This quantity will in fact be used subsequently except in special instances. Eqns.(13) and (14) can be formulated similarly.

Thus the problem of the determination of the rate of decomposition of chemically unstable bonds in the polymer under the influence of corrosive media reduces to the simultaneous solution of Eqns.(12)–(14).

Boundary Conditions

The following boundary conditions are usually encountered:

(a) the concentration of the diffusing substances on the surface of the polymeric article is constant. In practice this condition holds when a solution with a constant concentration of the diffusing corrosive medium flows rapidly around the article.

(b) The concentration of the diffusing substances on the surface of the polymeric article is a function of time, and

The following simple relation has been established with the aid of computer calculations:

$$\varphi(y) = 0.589 y^{1/2},$$

so that

$$c_n = \frac{4}{\pi^{1/2}} k_{\text{eff}}\, c^0_{\text{Cat}}\, D^{1/2}_{\text{Cat}}\, t^{3/2} l^{-1}, \tag{26}$$

i.e. during the initial period of the degradation the concentration of the ruptured bonds depends on the rate constant for the chemical reaction, the diffusion coefficient, the solubility of the catalyst, the thickness of the film, and time.

c. Internal Kinetic Region

The kinetic equation for this region can be obtained from Eqn. (24) with $y \gg 1$. This case obtains either for very thin films or very long times when the film has been saturated by the catalyst solution:

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}} t \left[1 - \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^4 y}\right]. \tag{27}$$

In this case one can restrict the treatment to the first term of the series, whereupon

$$c_n = k_{\text{eff}}\, c^0_{\text{Cat}} t. \tag{28}$$

Thus the concentration of the ruptured bonds corresponding to low degrees of conversion is proportional to the rate constant for the chemical reaction, the catalyst concentration under saturation conditions, and the reaction time.

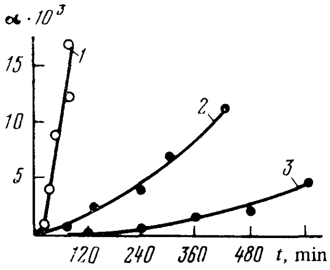


Figure 12. Time variation of the degree of conversion of ester linkages in the degradation of PETP films of different thickness in 53% H_2SO_4 at 116°C; film thickness (μm): 1) 5 ± 1; 2) 20 ± 2; 3) 80 ± 5.[81]

Fig. 12 illustrates the variation of the degree of conversion of the ester linkages α during the degradation of poly(ethylene terephthalate) (PETP) films of different thickness as a function of time[81]. For films 5 μm thick, there is a linear relation between α and time t starting from 30 min (by this time, the film has been saturated with the catalyst solution). Using Eqn. (28), we find the product $k_{\text{eff}} c^0_{\text{cat}}$. D_{cat} is determined from Eqn. (26) (Fig. 13).

We shall now consider certain characteristics of the degradation processes in the internal diffusion-kinetic and kinetic regions.

The Accessibility of the Functional Groups in Polymer Degradation Reactions

In polymeric materials with inhomogeneous structures (this applies primarily to heterophase systems), difficulties are frequently encountered in the definition of the terms "reactivity" and "accessibility" of the functional groups, because both terms are used to define the ability of the polymer to enter into a chemical reaction.

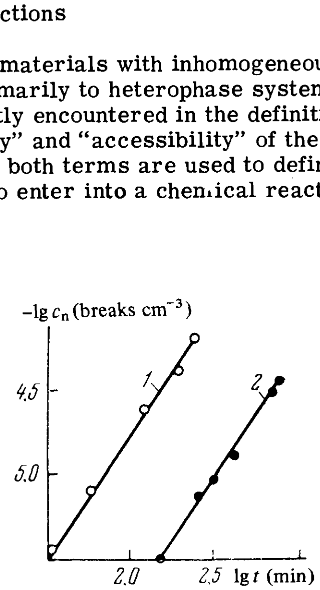


Figure 13. Variation of lg c_n with lg t for the degradation of PETP films of different thickness (1) in 53% H_2SO_4 at 116°C; thickness (l, μm): 1) 20 ± 2; 2) 80 ± 5.[81]

As already stated, the reactivity of the functional groups of the polymer can be accounted for on the basis of polar, resonance, and steric effects, and in most cases can be predicted quantitatively with the aid of correlation equations or by studying the kinetics of low-molecular-weight model reactions under corresponding conditions. Although there are as yet no rigorous quantitative data, presumably there should be no significant differences between the reactivities of the functional groups in regions with different structural inhomogeneities.

The accessibility of the "polymer" functional groups to molecules with which they should react is usually expressed quantitatively by the ratio $d = N/N_0$, where N_0 and N are respectively the total number of functional groups and the number of the accessible groups. It is reasonable to suppose that d will depend on the external conditions and on the method of determination. One should bear in mind that the "inaccessible" functional groups are involved in degradation reactions, but the rates of these reactions are low owing to the low concentration of the corrosive medium around these groups.

For polymers with mobile hydrogen atoms, a convenient method whereby the accessibility of the functional groups can be determined is provided by the H–D reaction, because during this reaction there is no change in the concentration of functional groups. The H–D exchange reaction has been investigated in detail in polycaproamide films[82,83]. The accessibility of the amide linkages is a function of temperature (Fig. 14). At 150°C all the amide linkages, including those in crystalline regions, are accessible to the H–D exchange reaction.

Most of the studies have dealt with the influence of the structure of cellulose on its reactivity in acid-catalysed degradation reaction[84]. The structure of the accessible regions in cellulose belonging to the structural type I has been studied in detail[85]. Small amounts of diethylaminoethyl substituents were introduced into the cellulose virtually without any alteration of the polymer structure (X-ray diffraction analysis was carried out); such substituents could be easily determined quantitatively in the soluble and insoluble products of the acid-catalysed hydrolysis by gas-liquid chromatography, which permits the determination of diethylaminoethyl groups in the 2-*O*-, 3-*O*-, and 6-*O*-positions of the D-glucopyranose residues.

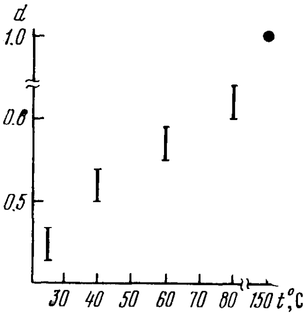


Figure 14. Temperature variation of the accessibility of the amide linkages in polycaproamide films.

The hydrolytic reaction takes place on the surface of the fibrils and there are two different types of accessible surfaces, called the "crystalline" and "disordered segments". According to BeMiller[86], the significant difference between the first-order rate constant for the formation of substituted D-glucopyranose residues in the acid-catalysed hydrolysis of cellulose at 25°C in 2.5 *N* HCl (Table 9) is due to the greater accessibility of the glycosidic linkages to protonation in the disordered segments and the greater ease of the transition from the chair to the half-chair conformation in these regions (the rate-limiting stage of the hydrolytic process).

Table 9. The first-order rate constants for the formation of various substituted D-glucopyranose residues in the acid-catalysed hydrolysis of cellulose at 25°C in 2.5 *N* HCl.[85]

D-Glucopyranose residue	Disordered segments; 10^3k, s^{-1}	Crystalline segments; 10^6k, s^{-1}	D-Glucopyranose residue	Disordered segments; 10^3k, s^{-1}	Crystalline segments; 10^6k, s^{-1}
Unsubstituted	1.1	6.5	3-*O*-Substituted	1.9	38.6
2-*O*-Substituted	4.8	15.8	6-*O*-Substituted	3.9	16,7

The distribution of the accessible surface between the disordered and crystalline segments, based on the content of the 2-*O*-substituted D-glucopyranose residues in these regions, is in the ratio 0.26 : 0.74 during the initial period of the reaction, changing to 0.36 : 0.64 as hydrolysis proceeds, because cellulose undergoes recrystallisation.

The surfaces of the crystalline and disordered segments of the fibrils are illustrated schematically in Fig. 15. In the crystalline regions (surfaces A and B), the segments are oriented and the hydroxy-groups are located in regularly repeating positions, the hydroxy-group in the 3-position being linked by a strong hydrogen bond to the oxygen in the ring of the neighbouring D-glucopyranose unit (Fig. 16). The bulk of the crystal structure defects due to twisting and bending of the fibrils and the presence of internal strain are concentrated in the disordered regions (surfaces C). The hydrogen bons 3-OH...5-O in these regions are least stable, which is the cause of the increase of the rate constant for the formation of 3-*O*-substituted D-glucopyranose residues.

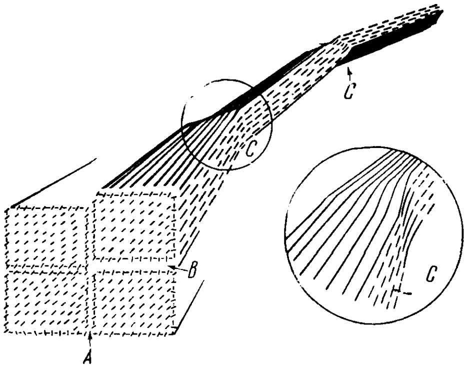


Figure 15. Schematic representation of the surfaces of the crystalline and disordered segments of cellulose fibrils[86].

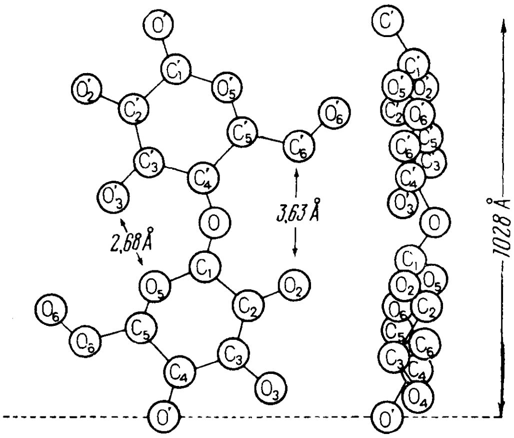


Figure 16. The conformation of the cellobiose segment of a crystalline cellulose chain[86].

Comparison of the Reactivities of the Functional Groups of Polymers in the Solid State and in Solution

Using as an example the degradation of cellulose derivatives, it is of interest to compare the kinetic parameters obtained for the solid state (degradation of ethylcellulose films in hydrochloric acid vapour)[76] and in solution (degradation of methylcellulose in aqueous hydrochloric acid solution)[61]. In the former case, the rate constants were calculated by Eqn.(28); ethylcellulose is an amorphous polymer and it was assumed that all the glycosidic linkages are equally accessible. In the latter case the rate constant under the conditions of an excess of hydrochloric acid was calculated from the equation for first-order kinetics but was referred to a single catalyst concentration (Table 10).

Table 10. Kinetic parameters of the acid-catalysed degradation reactions of methyl- and ethyl-cellulose.

Polymer	$k_{35°}$, mole $\min^{-1}$ cm^{-3}	E, kcal mole^{-1}	$\Delta S^{\neq}$ e.u.
Methylcellulose	$5.0 \cdot 10^{-6}$	30	4
Ethylcellulose	$1.2 \cdot 10^{-1}$	5.5	50

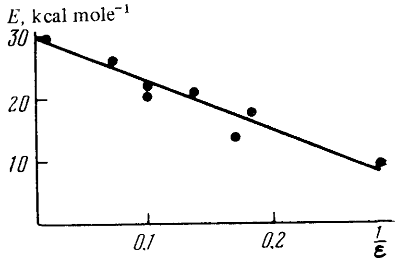


Figure 17. Variation of E with $1/\epsilon$ for the degradation of cellulose derivatives in various media[76].

To a first approximation, one may assume that the degradation of ethylcellulose takes place in "solution"; it is of interest to discover which properties of the solution are primarily responsible for the change in the kinetic parameters. Fig. 17 illustrates the variation of the activation energy for the degradation of cellulose ethers in various media as a function of the reciprocal of the dielectric constant[76]. The activation energy varies in opposition to $1/\epsilon$. Hence it follows that the chemical degradation processes in the solid state can be apparently simulated by reactions in solvents with similar physical parameters. To what extent this approach is valid will be established in the future when sufficient examples have accumulated.

d. The External Diffusion-kinetic Region

The degradation process in this region starts from the surface of the polymeric article. In this case we have

$$\frac{dc_n^S}{dt} = k(c_n^0 - c_n)^S c_{\text{Cat}}^S c_{\text{solv}}^S.$$

The superscript S denotes concentrations in the surface layer.

Regardless of the type of decomposition of the polymeric molecules, we have $(c_n^0 - c_n)^S \simeq (c_n^0)^S$. The state of the solvent and catalyst molecules in the surface layer has not been discussed in the literature. To a first approximation, one may assume that, under the conditions of adequate mixing, the thermodynamic parameters of the solvent and the catalyst in the surface layer and in the bulk of the liquid phase will be similar, so that

$$c_n^S = k_{\text{eff}}^S c_{\text{Cat}}^V c_{\text{solv}}^V,$$

where $k_{\text{eff}}^S = k(c_n^0)^S$ and the superscript V denotes bulk-phase concentration.

We shall consider how the mass of the polymer changes during degradation in this instance. Regardless of the type of decomposition of the polymer molecules, one can formulate an expression for the mass of the monomers formed:

$$m = k_{\text{eff}}^S c_{\text{Cat}}^V c_{\text{solv}}^V \, t \, S,$$

where S is the area of the polymer film. The thickness of the polymer film varies in accordance with the equation

$$x = l - \frac{k_{\text{eff}}^S c_{\text{Cat}}^V c_{\text{solv}}^V \, t}{\rho},$$

where ρ is the density of the polymer. The total decomposition time of the film is

$$\tau = \frac{m_0}{k_{\text{eff}}^S c_{\text{Cat}}^V c_{\text{solv}}^V \, S}.$$

The change in the mass of the polymer m_{pol} is described by the equation

$$m_{\text{pol}} = m_{\text{pol}}^0 \left(1 - \frac{t}{\tau}\right) = m_{\text{pol}}^0 \left(1 - \frac{k_{\text{eff}}^S c_{\text{Cat}}^V c_{\text{solv}}^V S t}{m_{\text{pol}}^0}\right). \quad (29)$$

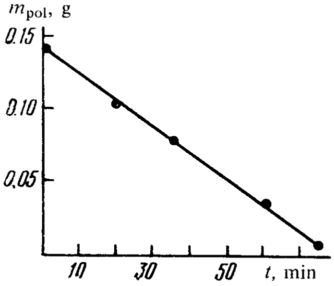


Figure 18. Time variation of the mass of the polymer in the degradation of a PETP film in 22.1% KOH solution at 88.2°C (l = 68 ± 8 μm, S = 14 cm²).[57]

When the degradation process takes place in the external diffusion-kinetic region, one must bear in mind that the polymer molecules in the surface layers have properties differing from those in the bulk of the specimen (molecular weight, degree of crystallinity, orientation, etc.). We have no data for the reactivities of polymer molecules in the surface layer. Progress in this field will be achieved by studying monolayers deposited directly on to the corrosive medium.

The change in the mass of PETP film during degradation is illustrated in Fig. 18. The following experimental observations have been made[57]:

(a) the reaction is of zero order with respect to the polymer;

(b) the molecular weight of the polymer film does not change until the end of the process;

(c) the multiple distorted total internal reflection infrared spectra contain no absorption bands due to the carboxy-groups formed in the decomposition of the ester linkages;

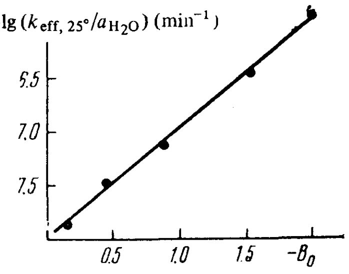


Figure 19. Variation of $\lg k_{\rm eff,25°}/a_{\rm H_2O}$ with the alkalinity function of aqueous potassium hydroxide solution for the degradation of PETP films 68 ± 2 μm thick[57].

(d) the values of $k_{\rm eff}^{\rm S}$ calculated by Eqn.(29) vary as a function of the thermodynamic parameters of the medium in accordance with Eqn.(9) (Fig.19), which describes the hydrolysis of low-molecular-weight compounds in aqueous solutions of alkalis.

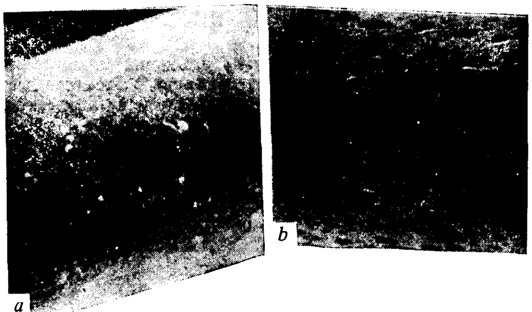


Figure 20. Photomicrographs (× 2100) [× 3000 in the Russian original] of PETP fibres during degradation in 22.1% KOH solution at 88.2°C: *a*) before degradation; *b*) after 5 min.

All these findings suggest that the reaction layer approaches a monolayer. The surface area of the films was estimated from profilograms. The variation of the surface area during the degradation process is illustrated in Fig.20. Photomicrographs of PETP fibres were obtained under a scanning microscope. In degradation of this type, structural gradients (degree of crystallinity and orientation) had almost no influence on the kinetic parameters.

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The concepts described above and the examples discussed reveal the fundamental characteristics of polymer degradation processes in corrosive media. The review deals with the degradation reactions in polymeric materials in an unstrained state in corrosive media which have been most thoroughly investigated—aqueous solutions of acids and bases. These constitute only some of the degradation processes encountered in practice. The creation and development of a theory of the chemical degradation of polymeric materials in the strained state in different corrosive media is one of the immediate tasks in the modern science of polymer degradation.

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The Present State of the Gas-chromatographic Analysis of Aminoacids

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Problems of the general and enantiomeric gas-chromatographic analysis of aminoacid mixtures are considered. Data are presented concerning the accuracy, reproducibility, and linear range of the determination of aminoacids. The applicability of various types of derivatives is investigated from the standpoint of the suitability for quantitative analysis. Since analysis of aminoacids includes, apart from the chromatographic procedure and the final integration, their isolation from the natural material and the preparation of volatile derivatives, particular attention is devoted in the review to errors at each stage of the analysis and their contribution to the resulting reproducibility of the analysis.
The review is of interest to persons working in the field of the chemistry of natural products, biochemistry, medicine, as well as specialists developing analytical methods associated with the preparation of volatile derivatives.
The bibliography includes 111 references.

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I. INTRODUCTION

Considerable advances have been achieved in recent years in the biochemistry and chemistry of proteins and aminoacids as a result of the application of modern analytical methods based on column and thin-layer chromatography. Nevertheless the search for more sensitive and accurate quantitative analytical methods is being continued. The principal trend in this search involves gas-liquid chromatography (GLC). Although conditions for gas-chromatographic analysis of general utility have not so far been found, it is already clear that the GLC of aminoacids is significantly more accurate than other methods, has an exceptionally low sensitivity theshold over a wide linear range, and is susceptible to full automation.

In contrast to an aminoacid analyser, the gas chromatograph is a universal instrument and can be used for the analysis of not only aminoacids but also of a multiplicity of other biochemically important substances of different types. A gas chromatograph can be very successfully combined with a mass-spectrometer, which gives rise to unique possibilities for the identification of minor components and anomalies in aminoacids. Finally GLC is the most accurate method for the analysis of mixtures of optical isomers (aminoacid enantiomers).

However, one must stipulate immediately that all the advantages of GLC in the analysis of aminoacids can be achieved only when instruments of sufficiently high quality are used. Thus relatively insensitive detectors, metallic columns with a high percentage content of the liquid phase, and coarse carriers combined with isothermal separation conditions were used in early attempts, these features being in general characteristic of the state of GLC at the end of the 1950's and the beginning of the 1960's. These studies showed that aminoacid derivatives are thermally unstable compounds with a wide range of vapour pressures and their analysis is therefore possible only on columns with a very low content of the [liquid] phase and very inert carriers and phases combined with programmed temperatures. This required the use of highly sensitive detection with a low noise level and compensation of background changes, which is best achieved with the aid of flame-ionisation detectors in compensation (two-column) schemes. Stabilised phases of the type of very pure polysiloxanes and polyesters as well as special carriers, ensuring minimal adsorption combined with a high homogeneity of the surface and the dimensions and shapes of the particles and lacking catalytic activity, have been widely employed. These are diatomaceous carriers such as Chromosorb W, Supelcoport, Anachrome, Gas Chrom, etc. The advantages of not only glass columns but also of a seamless separating channel became apparent.

Overall, it became clear that the gas chromatography of aminoacids is one of the most difficult ("delicate") chromatographic tasks and is comparable in its complexity and requirements with regard to equipment and materials perhaps only to the GLC of steroids. In view of the complexity and importance of such tasks, special chromatographs began to be manufactured in recent years for their solution (the so called chromatographs of the biomedical class), which constitute the highest achievements of chromatographic engineering in a certain sense as regards the rationality [of the design] and the quality of the separating channel.

This does not of course imply that satisfactory results cannot be achieved on ordinary industrial or home-made apparatus of suitable design. It is important that such apparatus should be provided with a seamless glass separating channel and a sensitive linear detector and should be based on a two-column scheme (for experiments with programmed temperatures). A unit for reproducible programming of the temperature, preferably with provision for the automatic return to the initial isothermal conditions, is essential. For quantitative analysis, the velocities of all the gases must be stabilised by accurate flow-rate regulators. Electronic integration combined with monitoring of the drift of the base line is necessary. In the latest studies carried out using modern research techniques, the most reliable results have of course been obtained.

Several reviews exist of the GLC of aminoacids[1-5] and the early studies are fairly fully described in Blau's review[3]. The authors of the present review endeavoured to examine as fully as possible the latest and most important data concerning the development of the GLC method for aminoacids, concerning both the separation and preparation of derivatives and problems of quantitative analysis. Unfortunately not all the published studies have been performed at a sufficiently high quantitative level. This remark applies also to published reviews, since they discuss mainly problems concerning the preparation of derivatives and their chromatography rather than the characteristics related to the accuracy, reproducibility, sensitivity threshold, and linear range, i.e. all the factors which constitute the subject of the present review, which deals with standard protein aminoacids. Anomalous aminoacids, and their iodine- and selenium-containing analogues, have been considered in the review of Coulter and Hann[6].

II. VOLATILE AMINOACID DERIVATIVES AND THEIR CHROMATOGRAPHIC SEPARATION

a. Standard Protein Aminoacids

Since aminoacids are virtually involatile thermally unstable compounds, their direct gas-chromatographic analysis is impossible. It is therefore quite natural that the main bulk of published work on the analysis of aminoacids by GLC consists of studies on their transformation into volatile substances suitable for separation. The majority of these studies have been carried out at a qualitative or semiquantitative level, covering more than eighty types of aminoacid conversion products (see, for example, Blau[3]). Many of the results are of merely historical interest. However, on the whole they are useful both as a source of ideas for the solution of specific problems and the development of new methods for the identification and quantitative analysis of aminoacids.

There are several publications on the pyrolytic GLC of aminoacids in which the feasibility, in principle, of analysis based on the hydrocarbon or amine "profile" of the thermal decomposition products has been demonstrated. However, the complications arising from the fact that the same pyrolysis products are common to different aminoacids and the side reactions between the aminoacids and their decomposition products require special laborious investigations of the pyrolysis of aminoacid mixtures using a complex mathematical technique for the interpretation of the results, so that this procedure is on the whole rather unpromising as a standard method for the quantitative analysis of mixtures[3].

The development of the analysis of aminoacids by GLC followed a different pathway, involving chemical transformations of aminoacids into volatile compounds on the "one aminoacid–one derivative" principle, but attempts to employ oxidative, reductive, and other transformations of aminoacids into compounds of other classes (amines, aldehydes, aminoalcohols, etc.) did not yield satisfactory results, primarily because the methods are insufficiently universal and quantitative. The most promising procedures proved to be those based on the protection of the carboxy- and amino-groups as well as other functional groups.

However, here too serious difficulties arise owing to the fact that natural aminoacids are substances of an extremely wide variety of chemical types, the common feature of which is merely the amino-group in the α-position relative to the carboxyl. For this reason, as noted by Blau[3], it is difficult to find modifying reagents and conditions for quantitative reactions involving the synthesis of volatile derivatives which are common to all natural aminoacids. It is no less difficult to find conditions for the separation of such non-homologous mixtures.

Experiment has shown that only a very few of the proposed derivatives are really suitable for a simple and reliable quantitative analysis, i.e. satisfy the essential requirements listed below:

(1) simplicity, quantitative yield of derivatives, reproducibility, and, if possible, rapid conversion of all the natural aminoacids in the mixtures;

(2) optimal volatility of the derivative, suitable for chromatography without losses;

(3) stability of the derivative during the experiment and storage under the usual laboratory conditions;

(4) stability under the conditions of the gas-chromatographic experiment, i.e. on contact with the liquid phase and the solid carrier at temperatures up to 200–250°C;

(5) the possibility of obtaining individual peaks on the chromatogram on the "one aminoacid–one derivative–one peak" principle.

Requirements (4) and (5) determine the accuracy and reproducibility of the chromatographic analysis proper and taken together determine the accuracy and reproducibility of the entire method.

At the present time only two types of derivatives which satisfy sufficiently fully the above requirements are known. These are some of the alkyl esters of *N*-acylated (usually *N*-perfluoroacylated) aminoacids and to a lesser extent trimethylsilyl (TMS) derivatives. Subsequently we shall consider mainly studies using such derivatives as well as derivatives of other types which have been published after the publication of the reviews of Blau[3] and Coulter and Hann[6].

In essence, the gas-chromatography of aminoacids has begun to develop on the basis of Fischer's study[7] of the separation of methyl esters of aminoacids by a fractionation procedure. In 1957 Bayer et al.[8] separated a mixture of such esters. They also pointed out[9] the suitability for GLC of *N*-trifluoroacetyl (TFA) derivatives of methyl esters of aminoacids. Since then derivatives of this type have been studied very intensively. Formyl, acetyl, trifluoroacetyl, pentafluoropropionyl, heptafluorobutyryl and other groups have been used in various combinations for the protection of the amino-group (and also OH and SH groups) in methyl, ethyl, propyl, butyl, isopentyl, and other aminoacid esters. At the present time only butyl esters of *N*-trifluoroacyl derivatives can be separated on filled columns satisfying at the same time requirement (5), which is in fact the reason for their exceptional importance in quantitative analysis. As a result of studies mainly by Gehrke's school and also Darbre, Blau, and Islan[10], the n-butyl esters of *N*(*O*, *S*)-trifluoroacylated aminoacids (*N*-TFA n-butyl esters)† and to a lesser extent the corresponding methyl esters[12] have come to be used most frequently. The conditions for the preparation of these derivatives, giving the highest yields, the possible complications due to the presence of impurities and the oxidising action of atmospheric oxygen, stability during storage and gas-chromatographic analysis, and also optimal separation conditions have been studied in greatest detail.

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†The *N*-TFA n-butyl esters have been proposed and separated for the first time by Zomsely et al.[11]

The alkyl esters of *N*(*O*, *S*)-acyl derivatives of aminoacids are usually prepared in two stages[13]. In the first stage, the aminoacid is converted into an alkyl ester by treatment with the corresponding alcohol in the presence of HCl. Methyl esters of aminoacids are also transesterified with higher alcohols[14]. After the removal of the excess reagent *in vacuo*, the product is acylated with a solution of the corresponding anhydride in methylene chloride, chloroform, or another suitable solvent.

It is noteworthy that new agents for the protection of functional groups have been discovered recently. In particular, Birkofer and Donike[15] recently suggested that bistrifluoroacetamide and its *N*-methylated analogue be used for trifluoroacetylation. The authors considered the application of these reagents in relation to various compounds, including certain aminoacids. The mildness of the acylation conditions, the possibility of obtaining mixed derivatives (the hydroxy-groups protected by trimethylsilyl groups are not affected during acylation), and the absence of the side reactions observed when trifluoroacetic anhydride is used have been noted among their advantages[16,17]. Both reagents are fairly volatile and emerge from the columns soon after the solvent.

The aminoacids must be freed from proteins, nucleotides, sugars, lipids, and other possible impurities before the synthesis of derivatives in the analysis of mixtures of natural products. Metal ions must also be eliminated, since most of them prevent a quantitative yield of the derivatives[18]. Furthermore, after entering the evaporator and the column, these ions catalyse the decomposition of the samples injected. The purification process and the complications arising in the analysis of aminoacids by GLC have been examined in detail[19].

The polyesters of ethylene glycol and neopentyl glycol with succinic, adipic, and sebacic acids exhibit the highest selectivity in the separation of the alkyl esters of *N*-acylaminoacids[13,20,21]. Neopentyl glycol sebacate, the phase with the highest thermal stability, is suitable for the separation of the *N*-TFA n-butyl esters of twenty protein aminoacids[21]. Columns with the mixed EGSS-X phase—diethyleneglycol succinate—have been used for the same purpose[22]. Polysiloxane phases (OV-1, OV-3, OV-7, OV-17, OV-25, OV-101, OV-210, OV-225, SE-30, SE-52, etc.) as well as their mixtures have been employed mainly for the analysis of mixtures containing heavy aminoacids, the separation of the derivatives of which on polar polyesters is difficult.

The majority of modern studies on the separation of *N*-TFA n-butyl esters culminated in the investigation by Stefanovic and Walker[23], who showed that the selectivity of columns with poly(ethylene glycol adipate) (PEGA) depends on the amount of phase deposited on the solid carrier. In particular, columns containing 0.65% of PEGA relative to the weight of the solid carrier (Chromosorb W) proved to be the most suitable for the separation of the *N*-TFA n-butyl esters of protein aminoacids (except tryptophan, arginine, histidine, and cystine). The optimal PEGA concentration for the separation of *N*-TFA n-butyl esters depends on the solid carrier employed—it amounts to 0.325% for Chromosorb G.[13]

Many modern studies on the separation of alkyl esters of *N*-acyl derivatives of aminoacids on columns with polar polyester phases with a low content of the phase have been carried out using a carrier heated to a specified temperature. Vitt et al.[24] showed that even a relatively inactive carrier, such as Chromosorb W, exhibits a sufficiently high capacity for adsorption, which is important for selective separation. It follows from the data in Table 1 that the free energy and enthalpy of solution on columns with a low content of the [liquid] phase are higher and that the order in which the *N*-TFA n-butyl esters emerge (i.e. the free energies of solution) under conditions of isothermal separation depends on the amount of the phase.

Table 1. The energies ΔG (kcal mole^{-1}) (at 126°C) and heats of solution ΔH (kcal mole^{-1}) (at 105–170°C) of the butyl esters of certain trifluoroacetylated aminoacids on columns with different PEGA contents on Chromosorb W(A.W.)[21].

Aminoacid	$-\Delta H$	$-\Delta G$	$-\Delta H$	$-\Delta G$
	0.8% PEGA		3% PEGA	
Glycine	15.0	5.5	14.9	5.4
Leucine	17.9	6.2	14.2	5.2
Methionine	20.2	7.4	18.0	6.9
Hydroxyproline	19.0	7.6	18.0	6.5
Phenylalanine	20.0	8.6	18.7	7.1

These data undoubtedly show that carriers with a low percentage of the phase behave in essence as modified sorbents a controlled selectivity of which is achieved by altering the content of the [liquid] phase or by heat treatment of the carrier. The separation on such carriers is sensitive to the type of temperature programme and the length of the chromatographic column. In particular, for a 3 m column with activated Chromosorb W, the optimal concentration ensuring the most effective separation of *N*-TFA n-butyl esters proved to be 0.58%[24] (for 1–1.5 m columns, Stefanovic and Walker[23] and Gehrke et al.[13] showed that the optimal PEGA concentration is 0.65%). The highest selectivity for a column length of 1.5–1.8 m is achieved at a rate of temperature rise of 2–4 K min^{-1} [13], while for a column 3 m long the optimum rate is 2–2.5 K min^{-1}.

According to our data, a change in the type of carrier for the stationary phase alters the nature of the separation. Presumably the future use of modified carriers of this type will extend the scope of the analysis of various volatile derivatives of aminoacids.

Gehrke et al.[25] proposed a scheme for the separation of *N*-TFA n-butyl esters of aminoacids based on the use of a single four-column apparatus or of two instruments, each comprising two columns. The first pair of columns with 0.65% of stabilised PEGA on Chromosorb W (A.W.), heat-treated for 12 h at 140°C, is used for the separation of *N*-TFA n-butyl esters of 17 aminoacids. The second pair of columns with 2% of OV-17 (OV-101) and 1% of OV-210 on silylated Chromosorb G is used for the separation of the *N*-TFA n-butyl esters of arginine, histidine, and cystine. Both pairs of columns can operate under the conditions of a single temperature programme and can therefore be combined in a single four-column apparatus, which permits the complete analysis of the protein aminoacids in a single cycle. The temperature programme is as follows: 70°C for 10 min followed by heating at a rate of 2–4 K min^{-1} to 235°C. The aminoacids are injected into the heated zone of the evaporator (at temperatures up to 240°C). According to the results of Vitt et al.[24], in the analysis of *N*-TFA n-butyl esters of aminoacids it is more convenient to employ a cold evaporator, having selected suitably the initial isothermal treatment.

Studies designed to choose conditions for the analysis of the *N*-TFA n-butyl esters of all twenty protein aminoacids on a single pair of columns are being continued. However, so far they have not been successful. Gerhrke and Roach[26] recently reported the analysis of the BTA derivatives of all twenty aminoacids on a single column with 10% of Apiezon M on Chromosorb W(HP), but, judging from the chromatograms presented, the separation of the *N*-TFA n-butyl esters was insufficient for accurate quantitative analysis; 13 peaks of the *N*-TFA n-butyl esters of protein aminoacids were incompletely separated.

The alkyl esters of pentafluoropropionyl and heptafluorobutyryl aminoacid derivatives, which became available subsequently, will probably prove more promising in this respect. Pollock and coworkers[27] were the first to suggest butyl esters of *N*(*O*, *S*)-pentafluoropropionyl derivatives of aminoacids and investigated their separation on silicone phases. Moss et al.[28] demonstrated the possibility of using n-propyl esters of heptafluorobutyryl derivatives of aminoacids. They carried out an analysis on a 3.6 m column with 3% of OV-1 on Chromosorb W(A.W.) treated with dimethylchlorosilane (DMCS), the temperature being programmed in the range between 100° and 250°C. In order to obtain a single histidine peak, the authors injected acetic anhydride together with the sample. We believe that, in order to convert monoacylhistidine into the diacyl derivative on the column, it would be necessary to inject together with the sample the anhydride used for the modification, as suggested for the first time by Gehrke and coworkers[29] for *N*-TFA n-butyl esters and as was done by Jonsson et al.[30] in the analysis of aminoacids in the form of the n-propyl esters of the *N*-heptafluorobutyryl derivatives.

Jonsson et al.[30] carried out the analysis on a short glass capillary column (6 m × 0.25 mm) to the walls of which a dimethylsiloxane polymeric phase has been grafted chemically. They achieved a satisfactory separation of derivatives of all the protein aminoacids except tryptophan; for the determination of cysteine, the latter was converted into the *S*-methyl derivative before modification.

Zanetta and Vincendon[14] demonstrated a satisfactory single-column separation of isopentyl esters of heptafluorobutyryl derivatives with the aid of 3% of SE-30 on Gas Chrom Q. Compared with *N*-TFA n-butyl esters, these derivatives are less volatile (which lowers the losses during evaporation), are less polar (which promotes a faster analysis), and give rise to symmetrical peaks.

Studies using alkyl esters of perfluoroacyl derivatives (particularly heptafluorobutyryl derivatives) lead at the same time to the possibility of a sharp reduction of the sensitivity threshold (down to 10^{-12}–10^{13} g) when an electron capture detector is used.

Despite the clear achievements in the separation and, as will be shown below, in the quantitative analysis based on esters of perfluoroacyl derivatives of aminoacids, the development of a single-stage method for the synthesis of volatile derivatives constitutes an attractive proposition. The studies by Rogozhin and coworkers[31], who showed that alkyl esters of *N*-acyl derivatives of aminoacids can be obtained in a single stage by condensing orthocarbonate esters with aminoacids, are of interest in this respect.

N- and *O*-Trimethylsilyl (TMS) derivatives can be obtained in a single stage. A fairly large number of studies have been made on the preparation and separation of TMS derivatives‡ of aminoacids[32-36]. In particular, new silylating agents have been proposed—bistrimethylsilylacetamide[36], bistrimethylsilyltrifluoroacetamide[34], etc.

These reagents give rise to a peak on the chromatogram which does not interfere with the peaks of the TMS derivatives of aminoacids. Furthermore, the use of bistrimethylsilyltrifluoroacetamide reduces the deposition of silica in the detector. The application of TMS derivatives of aminoacids in quantitative gas-chromatographic analysis is hindered by the fact that certain aminoacids form a mixture of silylation products, the proportions of which depend on the nature of the solvent employed[34].

In order to carry out the analysis of twenty protein aminoacids on a single column, Hardy and Kerring[37] used mixed derivatives—n-butyl esters of the *N*(*O*, *S*)-trimethylsilylated acids. The entire analysis on a ~2.5 m glass column with an internal diameter of 2 mm, filled with textured glass beads containing 0.2% of OV-7, was performed in less than 35 min.

The authors note that, in contrast to the free aminoacids, methylene chloride may be used as a solvent for the n-butyl esters in the silylation stage. On the one hand, the guanidino-group of arginine and the ω-amino-group of lysine are silylated under these conditions, which makes it possible to analyse the aminoacids, and, on the other hand, one can avoid the formation of the tristrimethylsilyl derivative of glycine, which emerges together with isoleucine derivatives during chromatography. However, as in the case of purely trimethylsilyl derivatives of aminoacids, the peaks of the serine and threonine derivatives are hardly separated at all, which naturally great complicates the quantitative analysis of these two aminoacids. Furthermore, the chromatograms show very small peaks corresponding to the trimethylsilyl derivatives of the non-esterified aminoacids, showing that the esterification reactions did not go to completion, which naturally constitutes an additional source of error in the analysis.

Thenot and Horning[38] used for GLC the alkyl esters of *N*-dimethylaminomethylene derivatives of aminoacids which are obtained in a single stage when *NN*-dimethylformamide reacts with aminoacid dialkyl acetals. They obtained derivatives of glycine, alanine, valine, leucine, isoleucine, aspartic and glutamic acids, phenylalanine, and lysine and separated them on filled and capillary columns with SE-30. We believe that, as long as the possibility of the rapid and quantitative formation of similar derivatives of "heavy" aminoacids (tryptophan, arginine, histidine, and cystine) has not been demonstrated, there is no point in trying to assess their practical value (with the exception, of course, of specific analytical problems). However, since the dialkyl acetals of *NN*-dimethylformamide do not react with hydroxy- and cercapto-groups under suitable conditions, the use of the above derivatives will always be limited.

The isopropylation of aminoacids has been recently proposed[39,40] as a single-stage reaction for the synthesis of derivatives to be used in GLC. However, these derivates have also scarcely found extensive applications, since satisfactory yields are obtained only for aminoacids without functional groups other than the carboxy- and α-amino groups. Furthermore, certain aminoacids give rise to several derivatives.

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‡ The separation was as a rule carried out on silicone phases.

Mitchell's suggestion[41] that the Schiff bases of aminoacids, obtained by coupling benzaldehyde or penta-2.4-dione to methyl esters of aminoacids be used for GLC, has also apparently not found many applications. It is hardly possible to extend this method to all the protein aminoacids and to achieve sufficiently reproducible results.

Williams and Halpern[42] suggested that the gas-chromatographic analysis of aminoacids be carried out by pyrolysing in the evaporator of the chromatograph the trimethylanilinium salts of *N*-neopentylidene derivatives of aminoacids. These salts are obtained in a single stage by reaction with 2,2-dimethylpropanal and trimethylanilinium hydroxide in methanol for 15 min and 80°C in the presence of 3 Å molecular sieves. After being injected into the hot evaporator of the chromatograph, they decompose with formation of the *N*-neopentylidene derivative of the methyl ester of the corresponding aminoacid. The hydroxy-groups are also methylated. The nitrogen atoms in the proline molecule and in the indole component of the tryptophan molecule are likewise methylated. The derivatives obtained were successfully chromatographed on a ~2.5 m stainless steel column filled with 0.5% of OV-17 on Chromosorb W(DMCS). However, in this case too it is impossible to chromatograph all the protein aminoacids: histidine does not yield a volatile derivative. Furthermore, arginine and cystine give rise to several products. Incidentally, we believe that these difficulties may be obviated by replacing the column and particularly the evaporator by components made of glass and by a careful selection of the pyrolysis temperatures.

Finally, one should note that in recent attempts to discover a convenient single-stage method for the synthesis of volatile aminoacid derivatives various investigators have again shown interest in the preparation of cyclic aminoacid derivatives. Thus Grahl-Nielsen and Solheim[43] investigated the chromatographic behaviour of various 2-alkyloxazolin-5-one derivatives of leucine [44,45] and showed that, although these substances are extremely reactive, nevertheless their thermal stabilities make them quite suitable for chromatographic analysis. The authors recommend 2-trifluoromethyloxazolin-5-one, obtained by the reaction of leucines with trifluoroacetic anhydride, as the preferred derivative for the separation of leucine isomers. However, we believe that it is hardly possible to obtain similar derivatives of more complex aminoacids and to achieve quantitative yields. Furthermore, the high volatility of the derivatives, which facilitates chromatogrphy, may lead to significant losses at the unavoidable stage involving the distillation of the trifluoroacetic acid formed.

Husek[46] used the reaction of aminoacids with dichlorotetrafluoroacetone, which also yields in a single stage analogous derivatives[47,48], in order to determine tyrosine and its mono- and di-iodo derivatives. The use of this reaction is probably still more limited, since in this case additional reactions are needed to protect the hydroxy-, ω-amino-, etc. functional groups. (Husek protected the hydroxy-group of tyrosine by reaction with perfluorobutyric anhydride). However, one should recall that similar derivatives with a large number of halogen atoms in the molecule make it possible to reduce sharply the sensitivity threshold when an electron capture detector is used and may therefore prove to be extremely useful in the solution of specific problems.

The interest in the GLC of thiohydantoin derivatives of aminoacids is noteworthy. In general, these derivatives are not very suitable for gas-chromatographic analysis but are important in connection with the determination of the primary structure of peptides and proteins by the method of Edman and Begg. We shall not consider problems concerning the analysis of these derivatives, since a fairly complete review by Pisano et al.[49] was published recently. Furthermore, the application of GLC for the determination of *N*-terminal aminoacids of proteins and peptides has been examined by Rosmus and Deyl[50]. Among the latest studies, the analysis of phenylthiohydantoins on short capillary columns is noteworthy[51].

b. Aminoacid Enantiomers

Two methods for the separation of enantiomers by gas chromatography are known at present. The first is based on the quantitative conversion of the enantiomers into diastereoisomers under the influence of a dissymmetric agent. The diastereoisomers are then separated on a usual chromatographic phase[52–54]. The other method is based on the use of a dissymmetric stationary phase[55].

Weygand et al.[53] achieved for the first time the separation of diastereoisomeric aminoacid derivatives by the GLC of dipeptides; at the same time the possibility of determining the enantiomeric purity and the configurations by the GLC method was demonstrated by a number of investigators using as an example the much more suitable *N*-trifluoroacetyl (*N*-TFA) derivatives of the diastereoisomeric aminoacid esters[56–63].

In particular, the present authors[63], Pollock et al.[59], and Gil-Av and coworkers[56] described in 1965 the separation of *N*-TFA derivatives of aminoacid esters using optically active s-butyl alcohol and menthol[61]. After this, numerous investigations of this problem were published[63–78].

As regards the determination of the configuration by the GLC method, one should note the relation between the elution order of the diastereoisomeric derivatives and their configurations established by a number of workers. Thus, it has been shown that, in a series of aminoacid esters[59,64,65], the diastereoisomers with the *RR*- and *SS*-configurations have the lowest energies of solution in the chromatographic phase and hence the lowest retention volumes, while the highest retention volumes are characteristic of the *RS*- and *SR*-forms. The 2-butyl ester of phenylglycine[64], a non-natural aminoacid, is an exception. It has been established, for a series of amides obtained from aminoacid esters and amines, $\mathrm{RCH(NHCOCF_3)CONH{-}\underset{\displaystyle R''}{\underset{|}{C}}H{-}R'}$ (R′ = alkyl and R″ = alkyl or COOR), that the *SS*-diastereoisomer is eluted after the *SR*-form.[66] According to the authors, the explanation is that the *SS*-structure of amides has a more open form, as a result of which the amide hydrogen in this structure is more accessible for interaction with the carbonyl group of the polyester phase (it has been established that such interaction occurs[66]).

Although the *N*-TFA derivatives of s-butyl esters of aminoacids can be separated on both filled[68,69,71] and capillary columns[59,61,64,65], in practice only capillary chromatography yields satisfactory results, i.e. results suitable for quantitative analysis, which is due to the low value of $\Delta(\Delta G)$ for the majority of the phases investigated[69] (Table 2). Another disadvantage of the separation of aminoacids in the form of the *N*-TFA derivatives of their s-butyl esters is the low availability of the optically pure s-butyl alcohol. On the other hand, the separation of diastereoisomers of this type makes it possible to analyse the enantiomers of heavy aminoacids, which is difficult in the case of the more bulky L-menthyl derivatives.

N-TFA-L-menthyl derivatives of aminoacids have very high values of $\Delta(\Delta G)$ (Table 3)[69], which makes it possible to use the usual (filled) columns[63]. The preparation of the derivatives constitutes the difficulty in this instance. The value of $\Delta(\Delta G)$ is partly influenced by the conformational immobility of the groups.

Table 2. The values of $-\Delta(\Delta G)$ (cal mole^{-1}) for the s-butyl esters of *N*-TFA derivatives of aminoacids (at 125°C) on different chromatographic phases.

Aminoacid	PEGA	PEG	NPGA
Alanine	44.0	57.0	42.0
Valine	52.0	44.0	44.0
Leucine	45.0	57.0	50.0
Isoleucine	70.0	86.0	55.0
Norvaline	35.0	52.0	32.0
Norleucine	47.0	44.0	32.0
α-Aminooctanoic acid	67.0	39.0	—

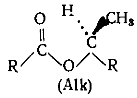
Note: PEGA = poly(ethylene glycol adipate), PEG = poly(ethylene glycol), and NPGA = neopentylglycol adipate.

In the chromatography of *N*-TFA-L-prolyl-2-methylindone, $\Delta(\Delta G^0) = 298$ cal mole^{-1}, which is the highest value noted in all instances of the separation of diastereoisomers, was obtained[72]. In this compound, the asymmetric centres are located in the ring, so that the conformational immobility of the groups linked to them is greater.

Table 3. The values of $-\Delta(\Delta G)$ (cal mole^{-1}) for the L-menthyl esters of *N*-TFA derivatives of aminoacids (at 160°C) on different chromatographic phases.

Aminoacid	PEGA	PEG	NPGA	APIEZON--L
Alanine	109.0	117.0	59.0	99.0
Valine	188.8	127.0	88.0	109.0
Leucine	145.0	—	124.0	108.0
Isoleucine	141.0	—	124.0	138.0
Norvaline	145.0	—	118.0	104.0
Norleucine	109.0	—	112.0	118.0
α-Aminobutyric acid	149.0	—	138.0	89.0

If the dissymmetric agent is acyclic, the groups linked to the asymmetric centre must be as large as possible. The point is that free rotation about the O–(Alk) bond in the molecule of the diastereoisomeric ester is hindered owing to the presence of the neighbouring carbonyl group.



When the substituent R′ is varied from CH_3 to t-C_4H_9, the separation is improved as a result of the decrease of the conformational mobility caused by the increase of the energy barrier to free rotation about the Alk–O bond[66,72].

As already pointed out, the other method for the gas-chromatographic analysis of enantiomers involves their separation on a dissymetric phase. The first reliable result was obtained by Gil-Av et al.[78] in 1967 in the separation of the ethyl, n-propyl, isopropyl, n-butyl, and 2-butyl esters of the *N*-TFA derivatives of alanine, valine, and leucine and the lauryl ester of *N*-TFA-L-isoleucine. Derivatives with a single asymmetric centre gave two peaks and those with two centres gave four peaks. The separation was specific: the methyl esters were not separated at all and only the cyclopentyl esters were fully separated.

Four types of dissymmetric stationary phases are now used for the gas-chromatographic analysis of enantiometric derivatives of aminoacids (Table 4):

I. Esters of *N*-TFA derivatives of aminoacids and C_6–C_{12} alcohols[78,79].

II. The ureide of the isopropyl ester of valine[55,80,81] (for the separation of amines and aminoacids).

III. Esters of *N*-TFA derivatives of dipeptides and C_1–C_6 alcohols[58,80–90].

IV. Amides[91,92].

The isopropyl esters of *N*-TFA-derivatives of aminoacids are most frequently separated. On peptide and ester L-phases, the D-isomer is eluted before the L-isomer, which makes it possible to determine the configurations of the aminoacids. On the ureide phase, the elution sequence of the enantiomers is related to the size of the alkyl substituents at the asymmetric centre and in the ester group of the enantiomer[80].

According to Gil-Av and coworkers[82,84,85], the mechanism of the separation process consists in the formation of diastereoisomeric complexes of the aminoacid enantiomer with the dissymmetric phase. It is suggested that the linkage between the molecules in these "complexes" is formed via hydrogen bond bridges. In other studies, hypotheses have been put forward concerning the structures of the "complexes" formed[79,84,85] and studies have been made in order to elucidate the role of the amide and ester components of the dipeptide[85,86,91] in the formation of the "complexes" with the enantiomeric aminoacid derivatives. Regardless of whether we attribute the dissolution of the aminoacid derivatives in the peptide phase to the formation of a "complex" or whether we explain the observed difference between the dissolution energies by specific solvation and a statistical distribution of different types of association, it is clear that the amide component of the dipeptide is in fact responsible for the stereoselective effect[86,91], although important secondary steric contributions are made by the ester end[85,86]. This is why tripeptide and even more so polypeptide phases proved to be less suitable for the separation of enantiomeric aminoacid derivatives than dipeptide phases[84,86].

Best results in the separation of aminoacid enantiomers (in terms of the highest values of $\alpha_{L/D}$[§]) have been obtained using dipeptide stationary phases of type (III), in which the hydrocarbon substituents at the asymmetric centres of the dipeptide and the ester groups are fairly bulky and branched (for example the cyclohexyl or t-butyl esters of the *N*-TFA derivatives of L-valyl-L-valine), and also on stationary phases of type (IV).

[§] $\alpha_{L/D}$ is the ratio of the retention volumes of the L- and D-enantiomers of aminoacids.

Table 4. The separation of derivatives of enantiomeric aminoacids on dissymmetric phases.

Aminoacids and their analytical forms	$\alpha_{L/D}$	Remarks
90°C; 50–100 m Pyrex column; d = 0.25 mm; chromatographic phase—lauryl ester of *N*-TFA-L-leucine [79, 82]		
2-Butyl esters of N-TFA derivatives of:		complete separation
D- and L-alanine	–	
D- and L-valine	–	
D- and L-leucine	–	
Methyl and ethyl esters of *N*-TFA derivatives of:		almost no separation
D- and L-alanine		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.001	poor separation
n-Butyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.012	inflection
Cyclopentyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.069	complete separation
100°C; 2 m × 1 mm column; 5% of chromatographic phase on Chromosorb W; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [80]		
t-Butyl esters of *N*-TFA derivatives of D- and L-alanine	–	in complete separation
110°C; 150 m × 0.5 mm steel capillary; He pressure 1.5 atm; chromatographic phase–cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82]		
Methyl esters of *N*-TFA derivatives of:		7 components out of 31 are not determined (the peaks are superimposed)
D- and L-alanine	1.067	
D- and L-aminobutyric acid	1.056	
D- and L-valine	1.031	
Glycine	–	
D- and L-threonine	1.053	
D- and L-n-valine	1.054	
D- and L-alloisoleucine	1.054	
D- and L-isoleucine	1.059	
D- and L-leucine	1.057	
D- and L-serine	1.045	
D- and L-norleucine	1.055	
D- and L-proline	1.044	
D- and L-aspartic acid	1.039	
D- and L-methionine	1.072	
D- and L-phenylalanine	1.082	
D- and L-glutamic acid	1.081	
110°C; 150 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82]		
Isopropyl esters of *N*-TFA-derivatives of:		
D- and L-Alanine	1.096	
D- and L-aminobutyric acid	1.089	
D- and L-valine	1.080	10 components out of 34 are not determined
Glycine	–	
D- and L-threonine	1.104	
D- and L-n-valine	1.095	
D- and L-alloisoleucine	1.097	
D- and L-isoleucine	1.077	
β-Alanine	–	
D- and L-leucine	1.114	
D- and L-serine	1.080	
D- and L-allothreonine	1.080	
D- and L-n-leucine	–	
D- and L-proline	1.041	
110°C; 30 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L- aspartic acid	1.062	
D- and L-methionine	1.116	
D- and L-phenylalanine	1.138	
D- and L-glutamic acid	1.123	
110°C; 120 mm × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82, 93]		
n-Butyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.087	4 components out of 23 are not determined
D- and L-valine	1.056	
Glycine	–	
D- and L-threonine	1.095	
D- and L-alloisoleucine	1.083	
D- and L-isoleucine	1.059	
D- and L-leucine	1.099	
D- and L-serine	1.079	
D- and L-proline	1.045	
110°C; 60 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82]		
n-Butyl esters of *N*-TFA-derivatives of:		
D- and L-methionine	1.110	
D- and L-phenylalanine	1.120	
D- and L-aspartic acid	1.060	
Table 4 cont'd.		
110°C; 120 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [82]		
3-Pentyl esters of *N*-TFA derivatives of:		6 components out of 27 are not determined
D- and L-alanine	1.130	
D- and L-α-aminobutyric acid	1.119	
D- and L-valine	1.090	
Glycine	–	
D- and L-threonine	1.100	
D- and L-alloisoleucine	1.116	
D- and L-isoleucine	1.098	
D- and L-serine	1.123	
D- and L-n-leucine	1.130	
D- and L-proline	1.039	
110°C; 60 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [93]		
3-Pentyl esters of *N*-TFA derivatives of:		
D- and L-serine	1.123	
D- and L-aspartic acid	1.083	
D- and L-phenylalanine	1.099	
100°C; 60 m × 0.25 mm glass capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-L-valyl-L-valine [93]		
Methyl esters of *N*-TFA derivatives of D- and L-alanine	1.080	
Ethyl esters of *N*-TFA derivatives of D- and L-alanine	1.106	
Isopropyl esters of *N*-TFA derivatives of D- and L-alanine	1.136	
t-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.207	
n-Propyl esters of *N*-TFA derivatives of D- and L-alanine	1.106	
n-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.113	
Cyclopentyl esters of *N*-TFA derivatives of D- and L-alanine	1.139	
107–109°C; 70 m × 0.25 mm glass capillary; chromatographic phase—isopropyl ester of *N*-TFA-L-valyl-L-valine [84]		
Methyl esters of *N*-TFA derivatives of D- and L-alanine	1.076	
Ethyl esters of *N*-TFA derivatives of D- and L-alanine	1.103	
Isopropyl esters of *N*-TFA derivatives of D- and L-alanine	1.126	
n-Propyl esters of *N*-TFA derivatives of D- and L-alanine	1.103	
t-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.214	
Cyclopentyl esters of *N*-TFA derivatives of D- and L-alanine	1.133	
139°C; 70 m × 0.25 mm glass capillary; chromatographic phase—isopropyl ester of *N*-acetyl-L-valyl-L-valine [84]		
Methyl esters of *N*-TFA derivatives of D- and L-alanine	1.072	
n-Propyl esters of *N*-TFA derivatives of D- and L-alanine	1.086	
t-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.130	
n-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.090	
Cyclopentyl esters of *N*-TFA derivatives of D- and L-alanine	1.095	
Isopropyl esters of *N*-acetyl derivatives of D- and L-alanine	1.103	
140°C; 120 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-phenylalanyl-L-leucine [83, 90]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.073	
D- and L-isoleucine	1.070	
D- and L-threonine	–	
D- and L-valine	1.045	
Glycine	–	
D- and L-leucine	1.083	
D- and L-serine	–	
D- and L-proline	1.00	
140°C; 30 × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-phenylalanyl-L-leucine [83]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-aspartic acid	–	
D- and L-methionine	–	
D- and L-phenylalanine	–	
D- and L-glutamic acid	–	
130°C; 10 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-phenylalanyl-L-leucine [83]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-phenylalanine	–	
D- and L-glutamic acid	–	
D- and L-tyrosine	–	
110°C; 120 m × 0.5 mm steel capillary; chromatographic phase—cyclohexyl ester of *N*-TFA-phenylalanyl-L-leucine		
Methyl esters of *N*-TFA derivatives of D- and L-leucine	1.082	
Isopropyl esters of *N*-TFA derivatives of D- and L-leucine	1.127	
t-Butyl esters of *N*-TFA derivatives of D- and L-leucine	1.176	
Methyl esters of *N*-pentafluoropropionyl (*N*-PFP) derivatives of D- and L-leucine	1.090	
Isopropyl esters of *N*-PFP derivatives of D- and L-leucine	1.123	
t-Butyl esters of *N*-PFP derivatives of D- and L-leucine	1.167	

Table 4 cont'd.

Aminoacids and their analytical forms	$\alpha_{L/D}$	Remarks
Methyl esters of *N*-heptafluorobutyryl (*N*-HFB) derivatives of D- and L-leucine	1.091	
Isopropyl esters of *N*-HFB derivatives of D- and L-leucine	1.129	
t-Butyl esters of *N*-HFB derivatives of D- and L-leucine	1.142	
Methyl esters of *N*-pentadecafluorooctanoyl (*N*-PDFO) derivatives of D- and L-leucine	1.100	
Isopropyl esters of *N*-PDFO derivatives of D- and L-leucine	1.137	
t-Butyl esters of *N*-PDFO derivatives of D- and L-leucine	1.177	
100°, 110°, 120°, and 130°C (the results are indicated in the corresponding sequence); 120 m x 5 mm steel capillary; chromatographic phase—cyclohexyl ester of L-norvalyl-L-norvaline[88]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.110	
	1.087	
	1.075	
	1.063	
D- and L-valine	1.083	
	1.069	
	1.050	
	1.044	
D- and L-isoleucine	1.108	
	1.093	
	1.079	
	1.068	
D- and L-leucine	1.100	
	1.096	
	1.082	
	1.070	
D- and L-α-aminobutyric acid	1.097	
	1.086	
	1.071	
	1.060	
D- and L-norvaline	1.092	
	1.081	
	1.070	
	1.060	
D- and L-norleucine	1.108	
	1.096	
	1.083	
	1.070	
D- and L-t-leucine	1.044	
	1.040	
	1.034	
	1.028	
100°C; remaining conditions—as above[88]		
Isopropyl esters of *N*-TFA derivatives of:		2 components out of 15 are not determined
D- and L-alanine	–	
D- and L-valine	–	
Glycine	–	
D- and L-threonine	–	
D- and L-isoleucine	–	
D- and L-leucine	–	
D- and L-serine	–	
D- and L-proline	–	
120°C; 122 x 0.508 mm steel capillary; chromatographic phase—cyclohexyl ester of the *N*-TFA derivative of the L-α-aminobutyric acid dipeptide[89]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-alanine	–	
D- and L-valine	–	
D- and L-threonine	–	
D- and L-isoleucine	–	
D- and L-leucine	–	
D- and L-serine	–	
D- and L-proline	–	
D- and L-aspartic acid	–	
Glycine	–	
D- and L-threonine	–	
145°C; 120 m x 0.5 mm steel capillary; chromatographic phase—caproylvaline *N*-n-hexylamide[90]		
Isopropyl esters of *N*-TFA derivatives of:		
D- and L-alanine	1.069	
D- and L-valine	1.047	
D- and L-n-valine	1.070	
D- and L-isoleucine	1.070	
D- and L-leucine	1.087	
D- and L-n-leucine	1.072	
130°C; 45 m x 0.5 mm steel capillary; chromatographic phase—*N*-lauroyl-L-valine-*N*-t-butylamide[91]		
Methyl esters of *N*-TFA derivatives of:		2 components out of 26 are not determined
D- and L-alanine	1.188	
D- and L-valine	1.170	
D- and L-threonine	1.177	
D- and L-t-leucine	1.084	
D- and L-alloisoleucine	1.186	
D- and L-isoleucine	1.159	
D- and L-leucine	1.280	
D- and L-proline	1.057	

Table 4 cont'd.

Aminoacids and their analytical forms	$\alpha_{L/D}$	Remarks
D- and L-serine	1.101	
D- and L-aspartic acid	1.078	
D- and L-glutamic acid	1.170	
D- and L-methionine	1.215	
D- and L-phenylalanine	1.198	
120°C; 80 m x 0.25 mm glass capillary; chromatographic phase—carbonylbis-(*N*-L-valine isopropyl ester) ureide[80]		
Esters $RCH(NHCOCF_3)CO_2R$ [$R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_7, iso-C_3H_7, or $CH(C_2H_5)_2$; the results are given in the same sequence] of:		
D- and L-alanine	1.017	
	1.031	
	1.034	
	1.039	
	1.042	
	1.046	
	1.060	
D- and L-α-aminobutyric acid	1.000	
	1.014	
	1.017	
	1.022	
	1.023	
	1.027	
	1.050	
D- and L-α-aminovaleric acid	0.976	
	0.994	
	0.997	
	1.002	
	1.004	
	1.005	
	1.030	
D- and L-α-aminohexanoic acid	0.968	
	0.985	
	0.989	
	0.994	
	0.997	
	1.002	
	1.027	
D- and L-α-aminooctanoic acid	0.956	
	0.973	
	0.977	
	0.979	
	–	
	0.990	
	1.016	
D- and L-valine	1.012	
	1.030	
	1.033	
	1.034	
	1.036	
	1.043	
	1.058	
D- and L-leucine	0.957	
	0.977	
	0.981	
	0.983	
	0.987	
	1.000	
	1.025	
D- and L-t-leucine	1.000	
	1.015	
	–	
	–	
	–	
	1.019	
140°C (the results are quoted in the same sequence); 17 m x 0.25 mm glass capillary; chromatographic phase—isopropyl ester of *N*-TFA-(L-valyl)$_2$L-valine (I) in mixture with isopropyl ester of *N*-TFA-L-valyl-L-valine (II)[84]		
t-Butyl esters of *N*-TFA derivatives of D- and L-alanine	1.288	$X^* = 0.42$
	1.269	$X = 0.42$
	1.242	$X = 0.28$
	1.239	$X = 0.42$
	1.216	$X = 0.55$
	1.214	$X = 0$
	1.205	$X = 0.28$
	1.206	$X = 0.42$
	1.203	$X = 0.55$
	1.187	$X = 0$
	1.180	$X = 0.28$
	1.179	$X = 0.42$
	1.176	$X = 0.55$
	1.165	$X = 0$
	1.156	$X = 0.28$
	1.159	$X = 0.42$
	1.154	$X = 0.55$
	1.142	$X = 0$
	1.139	$X = 0.28$

* $\frac{n_1}{n_1 + n_2}$; n_1 and n_2 are the numbers of moles of (I) and (II).

It has been shown that the structure of the volatile aminoacid derivative is important for the separation[84,85,88,91]. Thus the following features were noted in the separation of isopropyl esters of *N*-TFA-aminoacids on the cyclohexyl ester of *N*-TFA-L-norvalyl-L-norvaline[88]:

(a) The successive increase in the length of the hydrocarbon group and the replacement of the isopropyl ester of *N*-TFA-alanine by the corresponding α-aminobutyric acid and norvaline derivative leads to a decrease of $\alpha_{L/D}$.

(b) The replacement of the protons in the methyl group of alanine (the same derivatives) by methyl groups gives rise to the following series in terms of $\alpha_{L/D}$ [83]:

alanine > α-aminobutyric acid > valine ≫ t-leucine

(c) For leucines, we have the following series in terms of the values of $\alpha_{L/D}$:

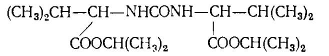
leucine, isoleucine > n-leucine ≫ t-leucine.

Parr and Howard[88] explained these characteristics by the steric hindrance in the formation of a complex with the chromatographic phase.

Proline, the *N*-TFA derivative of which does not contain amide hydrogen, yields the lowest separation factor among all the aminoacids on the available chromatographic phases[91,93]. The separation of aspartic acid enantiomers is also comparatively poor[93] (which cannot be said about glutamic acid).

All the volatile aminoacid derivatives which are capable of satisfactory resolution into enantiomers contain the group $-CONH\overset{*}{C}HR-CO-$. The quality of the separation is closely related to the presence of this structure[84], as shown by the finding that, on the isopropyl ester of *N*-TFA-L-valyl-L-valine, *N*-TFA-2-aminoheptane gives rise to only a slight inflection, while the isopropyl esters of *N*-(2,2,2,-trifluoroethyl)alanine [$CF_3CH_2NH-CH-COOCH(CH_3)_2$] and *N*-TFA-$\beta$-aminobutyric acid are not resolved at all[82]. According to the authors, these derivatives do not form "complexes" with the chromatographic phase and are involved in three hydrogen bonds. The statistical weight of the selective association of dipeptides (which have a high capacity for the formation of hydrogen bonds) via two or three bridges, for example in the case of *N*-TFA-2-aminoheptane, is very low[84].

Whereas the presence of the group –CO–NH–HCR–CO– (the acceptor and donor sections are located on either side of the asymmetric centre) is required for separation on a peptide phase, the presence of the group $-CO-NH-\underset{|}{\overset{|}{C}}{}^{*}$ is sufficient for the urea derivative obtained from L-valine,



$$\underset{\displaystyle\diagup \atop \displaystyle COOCH(CH_3)_2}{(CH_3)_2CH-CH}-NHCONH-\underset{\displaystyle | \atop \displaystyle COOCH(CH_3)_2}{CH}-CH(CH_3)_2$$

on which both amines and aminoacids can be separated[80]. Here it is significant that the elution sequence of the D- and L-isomers of the aminoacid derivatives $RCH(NHCOCF_3)CO_2R'$ is influenced only by the size of the R and CO_2R' groups and to a certain extent by the degree of branching of the hydrocarbon substituents.

Tripeptide phases have been used to separate enantiomers[84,86]. Here the working temperature is higher by about 10 K than the working temperature of the dipeptide phase and the separation factor is slightly lower. Furthermore, tripeptide esters can be used to make up binary phase compositions with m.p. <80°C.

Polypeptide phases have also been investigated; the separation on such phases proved to be poor, so that they can be scarcely used for the practical separation of enantiomers[86].

N-Pentafluoropropionyl and *N*-heptafluorobutyryl derivatives of dipeptide esters can be used to separate aminoacid enantiomers[86], while the corresponding *N*-acyl derivatives of aminoacid esters are more stable[85], the separation factors on these phases are higher, and the retention times are shorter than for the corresponding *N*-TFA derivatives[92].

The heats of reaction of the enantiomers with the dipeptide phases have been published in the literature[84,88,90,94]. For example, $\Delta(\Delta H)$ for the enantiomers of the *N*-TFA derivatives of the isopropyl esters of a number of aminoacids have the following values on the cyclohexyl ester of *N*-TFA-L-norvalyl-L-norvaline[88]:

Aminoacid	Aniline	α-Aminobutyric acid	Valine	Norvaline	Leucine	Isoleucine	t-Leucine
$-\Delta(\Delta H)\pm$ ±5, cal mole^{-1}	342	339	302	293	366	348	156

Table 4 lists the aminoacid derivatives and the phases used in the enantiomeric analysis of aminoacids on dissymmetric phases.

Summarising the results published hitherto concerning the use of dissymmetric phases for the separation of aminoacids, the following factors must be noted particularly.

1. The differences between the excess energies of the interaction of enantiomeric aminoacid derivatives with the phases described in the literature range from several cal mole^{-1} to 150 cal mole^{-1} depending on the enantiomer–chromatographic phase pair selected and the experimental temperature (values calculated from the retention parameters)[93].
2. Effective separation of aminoacid enantiomers during a reasonable period is possible despite the fact that high values of $\alpha_{L/D}$ are obtained on capillary columns only (Table 4).
3. The attainment of effective separation of enantiomeric pairs has in many instances been accompanied by the superposition of the peaks of several aminoacids belonging to different enantiomeric pairs despite the large number of phases tested (Table 4).
4. Unfortunately, many phases have a narrow working temperature range (the lower limit of the range is determined by the melting point of the phase and the upper limit by its volatility or instability).

Gas-chromatographic determination of the enantiomeric composition of complex mixtures makes it possible to solve also the specific problem involving the determination of optical purity. In both instances gas chromatography has an undoubted advantage over polarimetry and NMR. This highly effective method of separation does not, in principle, entail a limit to the number of components of the mixture of both optically active and inactive components being analysed.

III. QUANTITATIVE ANALYSIS

Quantitative analysis is characterised by parameters such as accuracy, reproducibility, linear range of concentrations being determined, and the sensitivity limit. For a multistage analytical procedure (and the GLC of aminoacids is in fact such a procedure), these parameters are determined by the partial parameters of each stage: the isolation of aminoacids from a natural or synthetic mixture, the formation of derivatives, the chromatographic separation proper, and the determination of the areas of the chromatographic peaks. Comparatively few studies have been made on the determination of these parameters[24,95-102] and those which have been carried out were mainly concerned with the separation of the butyl esters of the trifluoroacetylated derivatives by the Stefanovic–Gehrke method[12,13] and trimethylsilane derivatives and the preparation of such derivatives.

a. Reproducibility of the Analysis

The literature data on this problem are the most numerous and contradictory (coefficients of variation $\bar{w}$ ranging from 0.02 to 35% are quoted). This is not unexpected—there is also a large scatter in data concerning the reproducibility of the ion-exchange analysis of aminoacids. The results obtained in the separation of aminoacid enantiomers in the form of the isopropyl esters of their *N*-TFA derivatives on the cyclohexyl ester of *N*-TFA-L-valyl-L-valine[95] under the conditions of isothermal separation on capillary columns, i.e. under conditions ensuring the optimum signal/noise and signal/drift ratios with adequate separation of the peaks and equal chemical stabilities and volatilities of the components separated, have been the most reproducible (to within 0.02%, Varian 480 integrator).

The reproducibility of the separation of aminoacids in the form of the butyl esters of their trifluoroacetylated derivatives is somewhat less satisfactory. According to the results of Vitt et al.[24], the separation of such esters of twelve aminoacids on a 3 m glass column with stabilised PEGA (0.58%) has $\bar{w}$ = 0.17 rel.% (Infotronics CRS-100 integrator), the error (as well as the error in the separation of the enantiomers) depending on the amount of the sample injected into the chromatograph (see subsection c of the present Section). According to Gehrke's data[96], the average chromatographic reproducibility for 19 aminoacids, obtained from three replicate determinations, is to within 1.3%. The chromatographic reproducibility of the separation of trimethylsilane derivatives is to within 1.1 rel.% (for 20 aminoacids) according to Gehrke et al.[33]

Talbot et al.[97] investigated the reproducibility of the calibration coefficients in the analysis of the butyl esters of trifluoroacetylated aminoacids and showed that the coefficients vary on passing from one column to another (even with the same chromatographic phase). Thus the calibration coefficients of the threonine differed from one another by a factor greater than 2.5. The reason for this may be that the author failed to reach the complete separation of the butyl esters.

There is no doubt that the dependence of the calibration coefficients on the properties of the column may be reduced under the conditions of unified procedures for the preparation of the columns and by improving the efficiency of the separation. According to the present authors' results (with α-aminooctanoic acid as the internal standard), the calibration coefficients for the majority of aminoacids vary on passing from one column with PEGA to another by not more than 3%, the variation increasing to 10% only for threonine and serine. The stability of the calibration coefficients was achieved by a reproducible preparation of the columns and their prolonged conditioning (for at least 60 h at 190–200°C in a stream of helium).

The reproducibility of the conversion and the degree of racemisation in the preparation of derivatives for enantiomeric analysis may be investigated on the basis of data for the final procedure—the gas-chromatographic separation. However, the best procedure for the synthesis of the butyl esters of trifluoroacetylated aminoacids (direct esterification–acylation) is as follows. A dry mixture of aminoacids (between 2 μg and 50 mg of all the aminoacids) is covered by 3 *N* HCl solution in thoroughly dry n-butyl alcohol and heated at 100°C for 15–35 min. The excess reagent and water are distilled off on a rotary evaporator or in a stream of pure nitrogen, the mixture being heated twice with anhydrous methylene chloride in order to remove the residual water. The acylation is carried out with a 10% solution of trifluoroacetic anhydride in methylene chloride at temperatures up to 150°C for 5–60 min. There is a wide range of conditions associated with the different reactivities and stabilities of various aminoacids. Thus, when the mixture does not contain isoleucine, 15 min is sufficient for esterification (the maximum yield of the n-butyl ester of tryptophan is also obtained under these conditions); the quantitative esterification of isoleucine requires an increase of the reaction time to 35 min. On the other hand, the n-butyl esters of certain aminoacids (particularly histidine) are trifluoroacetylated quantitatively at a sufficient rate only at 100–150°C.[13]

The literature data for the preparation of the butyl ester of trifluoroacetylated histidine are contradictory (see, for example, the review of Coulter and Hann[6]). Even the structure of the volatile derivative is unknown. In view of the difficulty of the direct determination of histidine in the form of the butyl ester of trifluoroacetylated derivative, its preliminary conversion into aspartic acid by ozonolysis was suggested[6]. For the same purpose, arginine may be hydrolysed to ornithine in the presence of arginase[6].

Other complications in the quantitative analysis of the butyl esters of trifluoroacetylated derivatives are associated with the fact that the prolonged esterification necessary for the complete conversion of all 20 protein aminoacids into their esters is accompanied by partial charring of tryptophan. Therefore the esterification conditions must be rigorously standardised as regards the concentrations and amounts of reactants, the duration of reaction, and temperature[98].

According to our results, the calibration coefficients for the majority of butyl esters of trifluoroacetylated aminoacids do not change on storage of the derivatives (at room temperature) in the presence of a 2% solution of trifluoroacetic acid in methylene chloride for two weeks; however, the butyl ester of trifluoroacetylated methionine decomposes rapidly under these conditions. Dilute aqueous solutions of methionine are also unstable. Therefore methionine-containing mixtures must be analysed rapidly.

Together with the rigorous requirements which must be met by the gas chromatograph (seamless glass separation channel, minimal contact with the metal in the path traversed by the gases between the end of the column and the flame, an absolutely dry and filtered carrier gas), it is suggested that special attention should be devoted to the purity of the vessels used, the quality of the rotary evaporator which must not contain metallic components, and the purity of the derivatives of the reactants and gases used in the synthesis.

Vitt et al.[24] reported that samples without histidine and arginine can be acylated quantitatively with a satisfactory reproducibility at room temperature by two treatments with trifluoroacetic anhydride (initially in the form of a 10% and then a 2% solution in CH_2Cl_2) with intervening distillation of the CF_3COOH formed and the solvent on a rotary evaporator.

The esterification of aminoacids by isopropyl alcohol is much slower than the esterification with n-butyl alcohol. Fig. 1 presents kinetic curves for the esterification of a number of aminoacids[95], from which it follows that there is virtually no complete conversion in the synthesis of these derivatives. The authors recommend that the esterification time be limited to 4 h, since after more prolonged esterification the change in the enantiomeric composition of the mixture in consequence of racemisation becomes comparable to the random chromatographic error.

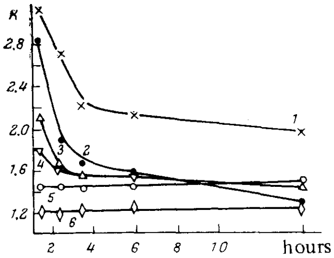


Figure 1. Dependence of the calibration coefficients of the isopropyl esters of *N*-TFA derivatives of aminoacids on esterification time; $K = S_{\mathrm{st}}(m_{\mathrm{i}}/m_{\mathrm{st}})s_{\mathrm{i}}$ (m_{i} is the aminoacid sample, m_{st} the sample of the standard, s_{i} the area of the aminoacid peak, and s_{st} the area of the peak due to the standard): 1) isoleucine; 2) valine; 3) threonine; 4) leucine; 5) glycine; 6) alanine.

In general aminoacid analysis, the reproducibility in the preparation of derivatives characterises the scope of the analysis of mixtures which do not require preliminary purification. The optimal overall reproducibility for two stages quoted in the literature[24] is $\bar{w}_{\mathrm{n}=4,\,\mathrm{m}=12} = 0.7\%$. According to the results of Gehrke and coworkers[96], the corresponding quantity for 19 aminoacids amounted to $\bar{w}_{\mathrm{n}=6,\,\mathrm{m}=19} = 1.5\%$. If the preparation of derivatives must be preceded by ion-exchange purification, the reproducibility of the analysis is impaired even more. Incidentally, this is no longer the "fault" of the gas chromatography—purification is a standard procedure also in analysis by ion-exchange chromatography.

Gehrke and coworkers[96,98] showed that the ion-exchange purification required for the isolation of the pure aminoacid fraction to be used in subsequent aminoacid analysis entails a partial loss of a number of aminoacids. The same workers established that arginine is completely lost in certain types of purification. The reproducibility of the gas-chromatographic analysis of synthetic and natural mixtures (urine, blood), obtained from three replicate determinations, amounted under these conditions to about 1.5% for synthetic mixtures and to 1.5–2.2% for natural mixtures. The reproducibility of the ion-exchange chromatography of the same specimens incorporating 17 aminoacids was to within 5–12%. Vitt et al.[24] obtained similar reproducibilities: 1.1% for the former case and 1.3% for the latter (for 12 aminoacids). Evidently the reproducibility of the ion-exchange purification is impaired for highly contaminated (natural) mixtures.

b. Accuracy of the Analysis

Strictly speaking the solution of the problem of accuracy is associated with the availability of standard procedures. Studies involving a standardisation procedure require standards whose purity approaches the reproducibility of the method and for this reason ion-exchange chromatography cannot serve as a standard for the determination of the accuracy of the gas-chromatographic analysis of aminoacids.

In all probability one must assume that gas chromatography itself constitutes the required standard procedure. The possibility of standardisation based on the equality of the concentrations of the compounds analysed was considered in the survey of Vitt et al.[95] Such instances include, for example, the equality of the concentrations of enantiomers in racemic mixtures. It has been shown that, in the chromatography of volatile D-aminoacid derivatives under isothermal conditions, a systematic error is observed, depending on the ratio of the peak variances and heights, i.e. on the concentration. This error is associated with the integration threshold—a sharp peak is integrated more fully than a broad peak. In the cases investigated the error was 0.02–0.3 rel.%.

When the internal standard method is employed (i.e. in general aminoacid analysis), the systematic error is determined by the purity of the standards and the operating point employed within the linear range of the method.

Under the conditions of large systematic errors which are known to exceed the uncertainty in the composition of the standards (this case is in fact characteristic of the stages involving the preparation of derivatives and particularly the purification on ion-exchange columns), the systematic errors can be readily determined from a small number of experimental results. This error (the average for 17 aminoacids) has been determined as 3.24 rel.% in the analysis of a standard mixture in the presence of urine aminoacids with removal of protein by ion-exchange[96]. The error can probably be reduced by extending the calibration over the entire analysis, including the purification stage.

In conclusion we shall consider the problem of the analysis of aminoacids in the case of overlapping peaks. The usual gas-chromatographic separation of the butyl esters of trifluoroacetylated aminoacids gives a satisfactorily resolved chromatogram for 18–20 natural aminoacids and is therefore suitable for an accurate quantitative analysis. Other methods, particularly the separation of enantiomers, where the number of peaks increases by a factor of two, do not exhibit this feature. The overall resolution depends in this instance on the separation of the components corresponding to various aminoacids and not on the selectivity of the separation within the enantiomeric pairs, i.e. is associated only with the efficiency of the column used. The reason is that the aminoacid mixtures are not homologous mixtures and therefore the retention volume of any one enantiomer of a single aminoacid may be close to the retention volume of other aminoacids. The likelihood of this situation increases with increase of the number of aminoacids present in the mixture. For a quantitative analysis of such partly resolved mixtures, simultaneous gas-chromatographic analysis on a column with a usual (not dissymmetric) stationary phase and the use of the available data for the aminoacid (but not enantiomeric) composition of the mixtures analysed has been suggested[95].

Then it follows from the experimentally demonstrated equality of the relative sensitivities of flame-ionisation detectors that

$$s_L + s_D = \omega s^*,$$

where $\omega = s_{\mathrm{st}}/s^*_{\mathrm{st}}$ is a proportionality coefficient, which remains unchanged for all the components in the given chromatographic experiment, s^* represents the peak areas for a column with a dissymmetric phase, s_{st} the peak area of the standard, and s the peak areas for a column with an optically inactive phase. Hence

$$\dot{S}_L = \omega s - \dot{s}_D.$$

In this case the systematic error depends on the accuracy of the determination of the peak areas under the conditions of chromatography on a usual phase.

c. The Linear Range and the Limits of Sensitivity

Depending on the concentrations being determined, the gas-chromatographic analysis of aminoacids in the form of the butyl esters of their trifluoroacetylated derivatives[13] is carried out using samples in the range 2 μg–50 mg. The size of the sample injected into the chromatograph then varies from 0.125 to 500 μg.

Chromatograms showing that individual peaks for 6–8 ng of aminoacids, injected into the gas chromatograph in the form of the butyl esters of their trifluoroacetylated derivatives, can be obtained using a flame-ionisation detector have been described in the literature[97]. In order to improve the signal/noise ratio, the bulk of the solvent vapour was discarded via a valve located between the analytical column and the fore-column[97].

According to the results of Vitt[110], the minimum amount of aminoacid which can be determined (in the form of the butyl ester of its trifluoroacetylated derivative) using an electron capture detector is 1–50 pg (evidently for a very narrow linear range).

It has been established[24] that the systematic and random errors in the gas-chromatographic analysis of the butyl esters of trifluoroacetylated aminoacids pass through a minimum (Fig. 2), i.e. there is an optimum concentration of the samples to be analysed as regards accuracy and reproducibility. The errors in the range of concentrations below the otpimum value are probably due to interference (noise and drift of columns), while the right-hand branch of the curve is due to the impairment of the resolution of the peaks with increase in concentration.

It follows from Fig. 2 that the linear range of the method is determined by the permissible concentrations and, conversely, the accuracy and reproducibility are determined by the linear range adopted and can be improved by operating within a narrower range of concentrations in the region of the minimum. The wide scatter of the literature values as regards accuracy and reproducibility is probably due to the fact that the investigators have not always worked in the concentration range corresponding to the optimum and also a satisfactory resolution and an adequately high signal/noise ratio were not always achieved. When the experimental parameters are incorrectly selected, the curve relating the errors to concentration is located at a higher level and has sharper minimum.

These limitations apply not only to the accuracy and reproducibility but also to threshold sensitivity: we are still unable to isolate aminoacids quantitatively and to obtain their derivatives at the level of 10^{-10} g.

Evidently relations between accuracy and reproducibility on the one hand and concentration on the other should also exist for processes involving the synthesis of aminoacid derivatives and the isolation of aminoacids from natural mixtures; in the region of low concentrations, there is a possibility of a sharp increase of errors owing to oxidation and residual sorption on glass and the materials of the columns[101]. One must recognise that, in a multistage procedure including gas chromatography, the stages preceding the gas chromatography proper are rate-limiting and have been least thoroughly developed.

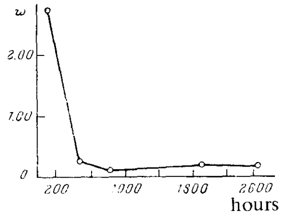


Figure 2. Variation of the reproducibility of the calibration coefficients of aminoacids with the concentration of the sample injected.

It follows from the above results that the accuracy and reproducibility of gas chromatography as a quantitative method are at least an order of magnitude higher than those of polarimetry and NMR in cases most favourable for these methods (in mixtures of two enantiomers, in determinations of optical purity). This can also be said of the sensitivity thresholds of the methods considered.

IV. EXAMPLES OF APPLICATIONS OF THE GAS-CHROMATOGRAPHIC ANALYSIS OF AMINOACIDS

In the first studies on the gas chromatography of aminoacids (see, for example, Gehrke et al.[13]), the analyses of natural mixtures (usually acid protein hydrolysates) were mainly carried out in order to demonstrate the applicability and reliability of the method, comparison with the results of ion-exchange chromatography being used as a criterion. As a result of numerous investigations, it became clear that the analysis of aminoacids by GLC is very accurate and reproducible and the number of studies in which GLC is used as an independent analytical method (not requiring a check by comparison with other methods) is at present increasing. Furthermore, certain investigations became possible (or at least became greatly facilitated) only after the application of the universal and highly sensitive gas-chromatographic method for the analysis of aminoacids.

We shall endeavour to demonstrate on a number of characteristic examples the present level of studies using GLC for the analysis of aminoacids and the scope of this method.

In 1971 Pellizzari and coworkers[13] used GLC to analyse blood plasma aminoacids in the form of the n-butyl esters of their *N*-trifluoroacetyl derivatives and carried out a statistical assessment of the results. They showed that only 0.2 ml of plasma is needed for the analysis and that the reproducibility of the results is quite satisfactory for clinical applications, for example for the diagnosis of metabolic disturbances (particularly in diseases associated with a disturbance of the aminoacid composition of proteins).

Subsequent studies confirmed the usefulness of GLC for the analysis of aminoacids in blood, urine, and other biological liquids in clinical tests.

For example the dynamics of aminoacid contents of the blood of patients operated on for cancer of the stomach and fed parenterally has been studied[69]. The aminoacids were determined in the blood plasma before the parenteral administration of the Aminosol preparation (1 g per kg of body weight in the form of a 10% solution) and in the course of its administration. It was found that the sum of the free analysable aminoacids in the blood plasma of the majority of the patients investigated decreased following the introduction of the aminoacid preparation into the blood supply, i.e. the injection of the mixture of aminoacids into blood accelerates sharply their assimilation. The blood plasma of the patients contained exclusively aminoacids having the L-configuration.

The increasing application of the GLC of aminoacids in biological studies is associated with the determination of the aminoacid composition and the primary structure of peptides and proteins and this is by no means the least important application. We have already noted[46] the success of the GLC of the thiohydantoin derivatives of aminoacids—the products of the stepwise degradation of proteins by the Edman method. The greater sensitivity of GLC compared with thin-layer chromatography makes it possible to use smaller amounts of the test substance and to determine the structures of proteins having higher molecular weights.

The advantages of gas chromatography may be even greater in the analysis of the composition of molecules of complex substances such as lipoproteins, protein–nucleic acid complexes, glycoproteins, etc. For example, Zanetta and Vincendon[14] showed that, in the case of glycoproteins, it is possible to analyse initially the hydrocarbon component and then the protein component of the same specimen. The universality of the GLC method is extremely convenient also in the analysis of products of aminoacid metabolism. Thus Albro and Fishbein[103] determined simultaneously with the aid of gas chromatography about 30 tyrosine and tryptophan metabolites—substances of very different chemical types.

In order to illustrate the scope of GLC in complex biological studies involving the determination of the aminoacid compositions, we may mention the study of Butler et al.[104], who used this method to analyse the aminoacids attached to tRNA.

Analysis of aminoacids by GLC has been used successfully in geochemical and paleontological investigations. Thus Pocklington[105] used this method for the quantitative analysis of the aminoacids in the water taken from the North Atlantic and Gardner and Lee[106] determined aminoacids in lake water. In both cases the aminoacid concentration was about 10^{-8} M (with respect to each aminoacid) and GLC proved to be a convenient and accurate analytical method. Gehrke's group[19] analysed the aminoacids in aqueous extracts of a specimen taken from the ancient Onverwacht chart (whose age is 3.4×10^9 years). GLC has demonstrated with a high degree of reliability the presence of aminoacids at the level of 10^{-8}–10^{-9} g. Bearing in mind that the minimum detectable amount of aminoacids has been reduced to 1–50 pg with the aid of the electron capture detector, the advantage of GLC in the analysis of aminoacids at an ultramicrolevel over other methods becomes clear. The new mass-spectrometric degradation method, usually called the "mass fragmentation" method, has a similar sensitivity limit. This technique has already been applied to the gas–liquid analysis of aminoacids in biological compounds[107] and in soil.

The unique possibility of determining by GLC the enantiomeric composition of aminoacid mixtures has been used in the analysis of collagen fossils[108], deposits on the sea bottom[109], and also the enantiomeric composition of the aminoacids in blood plasma and the hydrolysates and autolysates of baker's yeast[110].

The GLC of aminoacids will undoubtedly find extensive applications in studies associated with the origin of life on Earth and the possibility of life on other celestial bodies. Thus Raulin et al.[111] used this method to analyse the aminoacids formed in the photolysis of a gaseous mixture simulating Earth's primitive atmosphere. They showed that, in a single chromatographic experiment, it is possible to analyse together with the twenty main protein aminoacids also at least 18 non-protein aminoacids, which is particularly important in the study of chemical evolution and gives to gas chromatography an important advantage over aminoacid analysers.

The gas-chromatographic method has been used to seek aminoacids and other organic substances in the lunar dust supplied by the American Apollo spaceships[19,100] and we believe it will undoubtedly prove suitable for the analysis of soil specimens taken from the planets.

In conclusion we may note that the literature concerning the uses of the analysis of aminoacids by GLC is extremely extensive. This also shows that the reliability of the method and its suitability for the usual tasks in aminoacid analysis and for the solution of special problems requiring a universal, highly sensitive, accurate, and reproducible analytical procedure have been adequately demonstrated.

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Kinetics and Mechanism of Electrode Reactions of Metal Complexes in Aqueous Electrolyte Solutions

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The kinetics and the mechanism of electrode reactions of metal complexes, which include rapid processes of reorganisation of outer and inner coordination spheres, are examined, and criteria for distinguishing between outer-sphere and inner-sphere mechanisms of the electrochemical stage are discussed. Published data provide the basis for a consideration of the mechanism of simple electrode reactions, uncomplicated by change in the composition of the inner coordination sphere of the reactant complexes, and of more complicated reactions, in which the composition of the inner coordination sphere of the complexes is partly or completely changed. Consideration is given mainly to electrode reactions of complexes containing electrochemically inactive ligands. A list of 258 references is included.

CONTENTS

I. INTRODUCTION

A central aspect of the kinetics of electrode processes, which is also the least studied, is the mechanism of the electrochemical stages, as well as the relation between the kinetic parameters of these stages and the properties of the reactant species, the electrode, and the medium. Discussion of the nature and the mechanism of the electrochemical and other stages of electrode reactions (in particular choice of a model for the transition state) must take into account available information on the kinetics and the mechanism of similar homogeneous reactions. The fruitfulness of such an approach has been noted several times [1-8] and has been confirmed experimentally [4,9-11] on several reactions of metal complexes. The relation between the rate constants of homogeneous and heterogeneous electron-transfer reactions of metal complexes has been discussed by several workers [5,12-17]. However, the vast quantity of data available on homogeneous reactions of metal complexes and their mechanism [18-30] are relatively little utilised in electrochemical kinetics. Nevertheless, such an approach is especially promising for studying the mechanism of electrode reactions of metal complexes, in particular for identifying the electrochemically active complexes directly involved in the electrochemical stage and the character of their interaction with the electrode [31]. One aim of the present Review is to illustrate this principle. The formal kinetics of the electrode reactions of metal complexes and diffusion hindrances have been discussed many times [4,32-34] and will not be considered in detail here. Nor will kinetic and catalytic currents be discussed, for they have been surveyed in monographs [33-36] and several reviews [4,32,37-39].

Attention will be paid mainly to electrode reactions of metal complexes complicated by outer-sphere association or by rapid reorganisation of the inner sphere, which may occur particularly in the adsorption of complexes on electrodes. Since it is important to compare the kinetic parameters of a cathodic process with those of the opposite anodic process in order to obtain sound conclusions as to the nature and mechanism of electrochemical stages of complicated electrode reactions [40-43], considerable attention will be paid to work on these lines. The Review discusses electrode reactions occurring in aqueous solutions and involving metal complexes formed by electrochemically inactive inorganic and simple organic ligands.

II. STATE OF METAL COMPLEXES IN ELECTROLYTE SOLUTIONS

Most investigations on homogeneous and heterogeneous reactions of metal complexes are conducted in the presence of foreign electrolytes. In concentrated solutions of so called "inert" salts the complexes exist as complicated aggregates [44-49], containing various numbers of ligands X, cations B and anions A of the supporting electrolyte, and water molecules. The total concentration of the frequently studied singly charged complexes MX_i, in which one central metal ion M^{z+} is accompanied by i ligands X, can be expressed†

$$[MX_i] = \sum_x \sum_y \sum_z [MX_i(B)_x(A)_y(H_2O)_z], \tag{1}$$

where the summation covers both inner-sphere and outer-sphere species. Published [50] concentration stability constants of complexes $\beta_i = [MX_i][M^{z+}][X]^{-i}$ are effective quantities describing complicated equilibria between various associated forms and species from which they are produced [44-49]. The diversity and varying reactivity of the complexes present in solutions are responsible for the complicated character of their reactions. Study of the mechanism of the latter should utilise the greatest possible variety of methods for determination of thermodynamic and kinetic parameters of the processes. Outer-sphere association can be conveniently studied on highly charged

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†The possible charge on the ligands and the metal complexes is omitted for simplicity. Henceforward water molecules forming part of the metal complexes will sometimes not be written out.

inert complexes of the type $Co(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$, in which substitution of outer-sphere ligands does not take place during a measurement[46-49].

Aggregates such as ion-pairs or outer-sphere complexes are formed by inner-sphere complexes with ions of the supporting electrolyte or with free ligands[45-51]. The term "ion-pairs" is applied to aggregates formed by the interaction of two oppositely charged ions, between which an interlayer of water molecules may be retained. If this is absent, so called "contact ion-pairs" are formed, whose stability may be determined not only electrostatically but also by specific donor-acceptor interactions. Contact ion-pairs in which a negatively charged inner-sphere complex is directly bound to a cation of the supporting electrolyte are essentially doubly charged complexes[47,48]. If a positively charged inner-sphere complex adds one or more anions of the supporting electrolyte or neutral ligands, outer-sphere complexes are formed, often characterised by specific interactions between outer and inner coordination spheres[45-49].

III. ELECTRODE REACTIONS OF METAL COMPLEXES AND THEIR STAGES

Electrode reactions occurring on electrodes are described by equations containing the initial species and the final products. Frequently only the inner sphere is taken into account in writing down the electrode reactions of metal complexes: i.e. electrochemical and inner-sphere chemical‡ stages are considered. This is partly due to insufficient study of outer-sphere association processes, which play an important part in many homogeneous[5,26-28] and heterogeneous[4,31] reactions, especially those involving highly charged species. Hence electrochemical kinetics must consider not only inner-sphere but also outer-sphere stages—the formation and break-down of ion-pairs and outer-sphere complexes, the rearrangement of outer-sphere solvent molecules, and other processes that may take place either in the bulk of the solution or at the electrode surface.

The isolation of electron-transfer stages from the overall reaction in the kinetic study of electrode and homogeneous redox reactions of metal complexes is based essentially on the Franck–Condon principle and Libby's principle of symmetry which follows from it[52,53]. According to the latter the electron-transfer stage involves complexes the structure of whose heavy particle (atomic nuclei) is intermediate between those of the ground states of oxidised and reduced reactant forms. Outer-sphere and inner-sphere electrochemical stages are distinguished by analogy with homogeneous electron-transfer reactions[4,5,7,31]. If surface atoms of the metal electrode are separated from inner-sphere ligands of electrochemically active complexes by one or more ligands (solvent molecules), an outer-sphere mechanism operates. If the surface metal atoms are directly bound to an inner-sphere ligand (ligands) of the electrochemically active complex or to its central ion, an inner-sphere mechanism operates[31] (e.g. in the ionisation of metal atoms).

Both inner-sphere and outer-sphere mechanisms may operate in the electrical reduction of complexes. With a slow electrochemical stage the rate of reduction of mononuclear complexes of a metal can in general be expressed

$$i=\sum_{j=1}^{n} k_j^0 [MX_j]_s \exp\left[-\frac{\alpha_j F(\varphi-\psi_1)}{RT}\right], \qquad (2)$$

where $[MX_j]_s$ is the concentration of electrochemically active complexes in the inner or outer Helmholtz planes, α_j is the apparent transfer coefficient, ψ_1 is the potential at the electrical centre of a reactant species in the transition state[54,55], φ the electrode potential relative to that of the reference electrode, and k_j^0 the rate constant. Under certain conditions, depending primarily on the nature of the reactant complexes, the material of the electrode and its potential, both inner-sphere and outer-sphere mechanisms may operate. If one type of complexes, e.g. the highest complexes MX_n, take part in the outer-sphere electrochemical stage, Eqn. (2) is converted into Frumkin's equation[54]

$$i=k[MX_n]\exp\left(-\frac{z_0F\psi_1^0}{RT}\right)\exp\left[-\frac{\alpha F(\varphi-\psi_1^0)}{RT}\right], \qquad (3)$$

where $[MX_n]$ is the bulk concentration of the complex MX_n and z_0 is its charge, while ψ_1^0 is the potential in the outer Helmholtz layer. Diffusion hindrances are assumed to be absent.

It is advisable to use the following criteria to distinguish between outer-sphere and inner-sphere mechanisms of the electrochemical stage[7,31]: (i) the effect of the structure of the double layer on the kinetics of the electrochemical reaction[54] is based on the use of Eqn. (3), which is valid for an outer-sphere mechanism and is widely employed in electrochemical kinetics[35,55]; (ii) a low rate of substitution of inner-sphere ligands in the complex and of species directly adsorbed on the electrode§ (in comparison with the rate of the electrochemical stage) indicates an outer-sphere mechanism; (iii) the kinetic parameters of the electrochemical stage should be more greatly dependent on the electrode material with an inner-sphere than with an outer-sphere mechanism, for specific interaction of reactant complexes with the electrode takes place with the former mechanism; and (iv) larger negative entropies of activation should be observed with an outer-sphere than with an inner-sphere mechanism (for similar reactions).

The last three criteria resemble those used in studying the mechanism of homogeneous electron-transfer reactions[6]. However, it must be stressed that conditions of formation of the transition state differ significantly between homogeneous and heterogeneous electron-transfer reactions involving inert complexes. If rapid electron transfer occurs between two inert complexes in solution, an outer-sphere mechanism is functioning[5,28,57]. With fast electrochemical reactions of inert complexes, however, both outer-sphere and inner-sphere mechanisms may operate, because of the lability of most ions and molecules (including solvent molecules) adsorbed directly on metal electrodes. Such a conclusion may be drawn from the generally sharp increase in mobility of inner-sphere ligands with decrease in degree of oxidation of the central metal ion, especially with singly charged cations[19,28]. Yet the formal charge per metal atom on the surface of a metal

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‡Chemical stages of electrode reactions are those involving the rupture and formation of chemical bonds but not those involving charge transfer, which would entail interconversion of oxidised and reduced forms. The adsorption of ions and molecules on electrodes, involving partial transfer of charge, can be regarded as heterogeneous chemical stages.

§Ions and molecules directly adsorbed on the electrode surface can be regarded as the "inner coordination sphere of the electrode"[56], and adsorbed species as inner-sphere ligands.

electrode, at the usual departures from the zero-charge point, is a small fraction of unity. A very low mobility has been established for oxygen adsorbed on platinum in the first and second monolayers in the range of potentials of the oxygen portion of the charging curve[58,59].

Two groups of electrode reactions can be distinguished: (i) in simple reactions the composition of the inner sphere of the complexes remains unchanged; (ii) complicated reactions involve change in the composition of the inner sphere. Assignment of an electrode reaction to a particular group may be based on the dependence of the equilibrium potential of the system on the concentration of an inner-sphere ligand (ligands) or on chemical analysis. If the equilibrium potential can be measured, its dependence on the concentration of inner-sphere and outer-sphere species can be used to establish the composition of the complexes present in solution and also the optimum conditions for kinetic measurements[60].

The usual division of electrode reactions of metal complexes into those involving and not involving chemical stages[4,33,34] is less convenient for the discussion of experimental results, since it requires a knowledge of the reaction mechanisms, which are often dubious and may vary with the experimental conditions.

IV. ELECTRODE REACTIONS UNACCOMPANIED BY CHANGE IN THE COMPOSITION OF THE INNER SPHERE

The change in the charge of an inner-sphere complex resulting from an electrode reaction leads to rearrangement of the outer coordination sphere. Hence the rates of the electrode reactions may be determined by the rearrangement of outer-sphere aggregates[7,31] and the structure of the surrounding solvent[12-15,61], by the structure of the electrical double layer, and by adsorption phenomena[35,55], as well as in certain cases by rearrangement of the structure of the inner sphere of the complex[4]. As a consequence of the high rates of outer-sphere processes[62,63] rearrangement of the outer sphere takes place under reversible conditions.

The composition and the stability of outer-sphere aggregates present in solution must be known in studies of the reaction mechanism of charged complexes. Such information is obtained by investigating the equilibria of the corresponding bulk processes, in particular by electrochemical methods[46-49,64-67]. The study of bulk outer-sphere processes is important not only for establishing the stoichiometry of the overall electrode reaction but also for assessing possible similar outer-sphere interactions, which may take place in the double layer and precede the electrochemical stage.

The reactivity of outer-sphere aggregates often differs significantly from that of the unassociated species[68-70]. One reason is provided by the different conditions of solvation (hydration) of the reactant species. In non-contact ion-pairs, which appear e.g. on the interaction of trebly and less strongly charged anionic complexes with hydrated cations of alkali and alkaline-earth metals[46], the electric field of the ion-pair probably[70] exerts an ordering influence on the water molecules surrounding the inner-sphere complex. This leads to inhibition of the activation of complexes such as $IrCl_6^{3-}$ [71-74] and $IrBr_6^{3-}$ [75,76] by hydrogen ions and ions of alkali and alkaline-earth metals, the effect increasing with the atomic mass and the cationic charge.

Similarly, outer-sphere ions may also influence the rates of electrochemical stages[70]. If the charge on an inner-sphere complex increases as a result of an electrochemical reaction, prior association of the initial complex with an oppositely charged ion should increase the rate of the electrochemical stage, since the structure of the solvent in the ion-pair will approach that of the solvent surrounding the reaction product. The cathodic reduction of anions on negatively charged electrode surfaces provides an example of such reactions, the rate increasing in the sequence $Li^+ < Na^+ < K^+ < Cs^+$ and with increase in the cationic charge of the supporting electrolyte[77-85,33-35,55].

If the charge on an inner-sphere complex ion decreases as a result of an electrochemical reaction, prior association of the initial complex with an oppositely charged ion should inhibit the electrochemical stage, since the structure of the solvent surrounding the "free" complex is closer to the structure of the reaction product (in comparison with the ion-pair). An example of this type of reaction is the cathodic reduction of inner complexes such as $Co(NH_3)_6^{3+}$, whose reactivity diminishes when they form ion-pairs with anions of the supporting electrolyte[4,86-89]. The need to allow for orientation of water molecules surrounding ion-pairs in the transition state of an electrochemical reaction, and the influence of this factor on its activation energy, have been noted previously[90]. The structure of the electrical double layer greatly affects the rate of the cathodic reduction of negatively charged complexes and other anions[55,77-85]. Several recent publications[91-94] have discussed the influence of this structure on the kinetics of electrode reactions complicated by the formation of ion-pairs in solution.

Iron(III)–Iron(II) System

With sufficiently large negative surface charges, at which anions are electrostatically repelled by the electrode, the polarograms for the reduction of $Fe(CN)_6^{3-}$ at a dropping mercury electrode in solutions containing alkali-metal cations obey Eqn. (3) and the corrected Tafel relation which follows from it[95,96]. The linear sections of these corrected relations yielded transfer coefficients α of 0.16, 0.17, and 0.19 for lithium, potassium, and caesium ions respectively[95]. The corrected Tafel relations for the reduction of $Fe(CN)_6^{3-}$, as for that of $S_2O_8^{2-}$, are independent of the nature of the negatively charged electrode[85,97]. It has recently been shown[98] that the corrected relations for the cathodic reduction of $Fe(CN)_6^{3-}$ coincide on negatively charged bismuth, cadmium, lead, and indium. Together with earlier results[85] this demonstrates the absence of specific adsorption of the reactant complexes, i.e. an outer-sphere mechanism of the electrochemical stage.

The effect of the nature of cations of the supporting electrolyte on the rate of cathodic reduction of anions is attributed[78-82] to specific adsorption of the cations on the electrode. The adsorbed cations attract the reducible anions: i.e. they act as "bridges", diminishing the electrostatic repulsion of the anions by the negatively charged electrode surface and thereby accelerating the process.

Alkali-metal cations exert a similar accelerating effect[99] in 1 M solutions of their chlorides when hexacyanoferrate complexes undergo charge transfer on a positively charged platinum electrode. The exchange current density i_0 of the complex system increases by factors of ~3 and 15 in passing from 1 M lithium chloride to 1 M sodium chloride and from the latter to 1 M potassium chloride respectively: i.e. effects are observed analogous to those occurring on negatively charged electrode surfaces (at cation concentrations of ~10^{-3} M).[95,96]

The great effect of the nature of the alkali-metal cation in 1 M solution on the rate of charge transfer between negatively charged iron complexes on platinum (Table 1) is probably due mainly to differences in the nature of the outer-sphere aggregates of oxidised and reduced forms present in solution. According to published results[46,100,101] the association of hexacyanoferrate(II) complexes with alkali-metal cations is accompanied by breakdown of the hydrate sheath of the cation, which does not occur with the oxidised complex. Thus among alkali-metal ions lithium ions form the most stable aggregates with hexacyanoferrate(II) ions, and the least stable with hexacyanoferrate(III) ions, since the radius of the hydrated cation increases on passing from caesium to lithium[102]. In accordance with this the concentration of electrochemically active iron hexacyanide complexes, which according to the Franck-Condon principle should have the same structure of inner and outer coordination spheres, will increase from lithium to sodium and then to potassium ions. This is obviously responsible also for the increase in rate constant k_S (in exchange current density) in the hexacyanoferrate system on passing from 1 M lithium chloride to 1 M potassium chloride (Table 1). This explanation is consistent also with the smaller effect of the nature of the alkali-metal cation on the rate of charge transfer between $Fe(CN)_5X^{2-}$ and $Fe(CN)_5X^{3-}$ complexes ($X = NH_3$, H_2O)[99] (Table 1), which, like other doubly and trebly charged complexes, probably associate with hydrated alkali-metal ions. The stability of the resulting ion-pairs increases in the sequence $Li^+ < Na^+ < K^+$.[46]

Table 1. Standard heterogeneous charge-transfer rate constants k_S for iron complexes* at 25°C.

System	Supporting electrolyte, M	k_S, cm s^{-1}	Ref.
Pt/$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	1KCl	0.24	103
	1LiCl	0.0032	99
	1NaCl	0.01	99
	1KCl	0.15	99
Pt/$Fe(CN)_5NH_3^{2-}$, $Fe(CN)_5NH_3^{3-}$	1LiCl	0.024	99
	1NaCl	0.032	99
	1KCl	0.08	99
Pt/$Fe(CN)_5H_2O^{2-}$, $Fe(CN)_5H_2O^{3-}$	1LiCl	0.0032	99
	1KCl	0.012	99
a—Ag/; *b*—Au/; *c*—Pt/$Fe(C_2O_4)_3^{3-}$, $Fe(C_2O_4)_3^{4-}$	$0.5K_2C_2O_4$ (20° C)	*a*—0.001; *b*—0.005; *c*—0.009	104
Hg/$Fe(C_2O_4)_3^{3-}$, $Fe(C_2O_4)_3^{4-}$	$1K_2C_2O_4$; $0.5H_2C_2O_4$	1.29	105

*Rate constants k_S for certain systems[99] were calculated from the exchange current density on the assumption that the sum of the transfer coefficients of cathodic and anodic processes is unity (transfer coefficients of the cathodic process α for the first and last systems above are respectively 0.50 [103] and 0.84 [105]).

Study of charge transfer in hexacyanoferrate and similar complexes of iron in 1 M solutions of foreign salts has revealed[99] a breakdown of the linear dependence of the exchange current density

$$\lg i_{ex} = \lg zFk_s + \beta \lg c_{ox} + \alpha \lg c_{red} \qquad (4)$$

on the concentrations of oxidised and reduced forms c_{ox} and c_{red} that follows from the slow-discharge theory. This is attributed[99] to the involvement of dimers—polymerisation products of iron(III) and iron(II) complexes—present in solution, in the charge-transfer processes. However, this conclusion is inconsistent with results[103] establishing the validity of Eqn. (4) over wide concentration ranges of hexacyano-complexes of iron(III) and iron(II). Values of k_S and α obtained in this work[103] agree with those of other investigators¶. The absence of appreciable quantities of dimers in hexacyanoferrate(III and II) solutions is indicated also by results for their homogeneous electron-transfer reactions[106], whose rates, however, are sensitive to the pH of neutral and nearly neutral solutions. A similar effect can probably occur on charge transfer in hexacyanoferrate complexes on electrodes. At a rotating graphite electrode[107] in the region of Tafel behaviour kinetic orders less than unity with respect to the reactant complexes are found, and apparent transfer coefficients of cathodic (0.2) and anodic (0.2) processes whose sum is significantly less than unity. In the vicinity of the equilibrium potential the apparent transfer coefficients are 0.5 on graphite[107] and platinum[103] electrodes. This indicates that the electrode potential has a significant influence on the conditions of charge transfer in relatively simple electrode reactions, uncomplicated by change in the composition of the inner sphere. It is concluded[107] that charge transfer in hexacyanoferrate complexes on graphite takes place in the adsorbed state.

The considerable dependence of the constant k_S on the electrode material found for charge transfer in trioxalato-iron complexes[104,105] indicates an inner-sphere mechanism of the electrochemical stage.

Cobalt(III)–Cobalt(II) System

Exchange current densities observed in charge transfer on a platinum electrode between higher complexes of cobalt(III) and cobalt(II) with ammonia[86,88,89], ethylenediamine (en)[87], diethylenetriamine (dien)[108,109], cyclohexanediamine (chn)[110,111], and phenanthroline (phen)[112] conform to Eqn. (4) provided that c_{ox} and c_{red} are the concentrations respectively of oxidised and reduced forms with the same composition of inner and outer coordination spheres and that the process suffers no retardation caused by adsorption of ligands, complexes, and their hydrolysis products. With increase in the concentration of a ligand X the exchange current increases initially owing to the formation in solution of higher complexes from lower complexes of the reduced form (e.g. of $Co\,en_3^{2+}$ from $Co\,en_2^{2+}$), and then either ceases to depend on [X] or decreases (with increase in the concentration of diethylenetriamine, cyclohexanediamine, or phenanthroline). This is attributed to adsorption of the organic diamines, which block part of the electrode surface. The adsorption of hydrolysis products of cobalt(III) complexes has a similar effect. Other workers have also established[113,114] the electrochemical inactivity of $Co\,en_i^{2+}$ complexes in which $i < 3$ in an electrode reaction involving $Co\,en_3^{3+}$ and $Co\,en_3^{2+}$ complexes.

Table 2 shows that k_S decreases on passing from a chloride to a sulphate supporting electrolyte, and with trisethylenediaminecobalt complexes in the sequence $Cl^- > Br^-$, $SO_4^{2-} > S_2O_3^{2-}$. This sequence applies to the increase in stability of the outer-sphere complexes formed by the interaction of $Co\,en_3^{3+}$ with anions of the supporting electrolyte[117,118], which according to what has been stated

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¶Table 1 gives values of k_S and α obtained[103] for the reduced surface of a platinum electrode. The values found for oxidised platinum are k_S = 0.028 cm s^{-1} and α = 0.46.

earlier in this Section are electrochemically less active than are the free Co en_3^{3+} complexes.

Information on the interaction of electrochemically active complexes of bi- and ter-valent cobalt with the electrode material is very limited. From an analysis of the Faraday impedance of the system comprising the complexes Co en_3^{3+} and Co en_3^{2+} with a mercury electrode Laitinen and Randles concluded[115] that both adsorbed and unadsorbed cobalt complexes take part in the reaction. From this it may be assumed that two mechanisms—inner-sphere and outer-sphere—operate in the electrochemical stage in this system. The close similarity in the values of k_S determined for trisethylenediaminecobalt and bisdiethylenetriaminecobalt complexes at mercury and platinum electrodes (Table 2) is consistent with the hypothesis that the electrochemical stage takes place either entirely or largely by an outer-sphere mechanism.

Table 2. Charge-transfer rate constants k_S and transfer coefficients of the cathodic process α for cobalt complexes at 25°C.

System	Supporting electrolyte, *N*	$10^2 k_S$, cm s^{-1}	α	Ref.
$Pt/Co(NH_3)_6^{3+}$, $Co(NH_3)_6^{2+}$	$1NH_4Cl+7NH_3$	0.0525	0.58	86
	$1(NH_4)_2SO_4+7NH_3$	0.021	0.59	88
$Hg/Co(en)_3^{3+}$, $Co(en)_3^{2+}$	$1NaClO_4+0.1$ en	9 (19° C)	—	115
$Pt/Co(en)_3^{3+}$, $Co(en)_3^{2+}$	$1NaClO_4+0.1$ en	2.9	—	87
	1KCl+0.1 en	2.1	0.24	87
	$1Br^-+0.1$ en	0.62	—	87
	$1SO_4^{2-}+0.1$ en	1.64	—	87
	$1S_2O_3^{2-}+0.1$ en	0.46	—	87
$Hg/Co(dien)_2^{3+}$, $Co(dien)_2^{2+}$	$NaClO_4$	14.7–43		116
$Pt/Co(dien)_2^{3+}$, $Co(dien)_2^{2+}$	1KCl+0.1 dien	7.7	0.23	108
$Pt/Co(chn)_3^{3+}$, $Co(chn)_3^{2+}$	1KCl+0.1 chn	0.075	0.23	110, 111
$Pt/Co(phen)_3^{3+}$, $Co(phen)_3^{2+}$	$1KCl+4\cdot10^{-3}$ phen	4.8	0.23	112

Values of k_S obtained for hexammine- and triphenanthroline-cobalt complexes (Table 2) and the rate constants of the corresponding homogeneous electron transfers conform[89,112] to the Marcus relation[12], which should hold for an outer-sphere mechanism. With the trisethylenediamine complexes, however, this relation is not satisfied, which is attributed[87] to a possible complicating influence on the electrochemical stage by either hydrolysis products or the electrode surface, which may change for instance[89] the spin multiplicity of the complexes. The high-spin and low-spin configurations respectively of the cobalt(II) and cobalt(III) complexes that predominate in solution ($t_{2g}^5 e_g^2$ and t_{2g}^6) compel rearrangement of the electronic configuration of the reactant complexes, which is responsible[†] for the slow transfer of electrons between cobalt(III) and cobalt(II) complexes having inner spheres of the same composition in homogeneous[20,28,121,122] and perhaps heterogeneous[4] electron-transfer reactions.

As the Marcus relation[12] between the rate constants of homogeneous and heterogeneous electron-transfer reactions is not obeyed in the Cr $bipy_3$–Cr $bipy_3^+$ system, other available data on the relation between electron-transfer rate constants have been discussed[123].

Other Systems

The heterogeneous rate constants k_S for the MnO_4^{2-}–MnO_4^- system at platinum, palladium, gold, and graphite electrodes (0.012, 0.0064, 0.008, and 0.02 cm s^{-1} respectively) and the corresponding transfer coefficients for the cathodic process (0.30, 0.30, 0.35, and 0.25), determined[124] with rotating disc electrodes in 1 M potassium hydroxide (at 20°C), are little affected by the electrode material. In view of this, the high k_S values, and the inertness of the complexes and oxygen atoms adsorbed in the region of the equilibrium potential of the redox system [0.610 V (n.h.e.) in 1 M sodium hydroxide[125]], at least in the case of a platinum electrode, it may be concluded that the electrochemical stage has an outer-sphere mechanism. Analysis of cathodic and anodic polarisation curves obtained for different concentrations of manganate and permanganate ions (in 1 M sodium hydroxide) indicated[125,126] that the electrochemically active complexes were in an adsorbed state, their adsorption on the electrode being accompanied by partial transfer of charge[55,127-137]. An outer-sphere mechanism of the electrochemical stage does not exclude specific interaction between electrode and species reacting on it (by analogy with outer-sphere complex formation in the bulk of the solution).

It is a complicated problem to establish the mechanism of electrochemical stages in the potential range corresponding to high rates of exchange with the solution of species directly adsorbed on the electrode. In such cases systematic investigations of the influence of the structure of the double layer, the material of the electrode, the nature of foreign electrolytes, and other parameters on the kinetics of the electrode reaction are necessary. Kinetic investigation of charge transfer between aquo-complexes of europium(III) and europium(II) at a mercury electrode in 1 M potassium chloride and iodide solutions, allowing for the effect of the structure of the double layer, indicates that electrochemically active complexes are localised in the region of the outer Helmholtz plane[138], i.e. that the electrochemical stage has an outer-sphere mechanism.

Comparison of the kinetic parameters of similar homogeneous and heterogeneous electron-transfer reactions may sometimes indicate the mechanism of the electrochemical stage. Thus the rate of reduction at a mercury cathode of the inert complexes $CoX(NH_3)_5^{2+}$ (where X is a singly charged anion) and other similar cobalt(III) complexes depends on the nature of the inner-sphere ligand X in the same way as does the rate of their reduction by the inert complexes $Ru(NH_3)_6^{2+}$. Since an outer-sphere mechanism operates in the latter case, a similar mechanism was deduced[10] for the reduction of cobalt(III) complexes at a mercury electrode. An outer-sphere mechanism for such electrochemical reactions had been suggested previously[4].

V. ELECTRODE REACTIONS ACCOMPANIED BY CHANGE IN THE COMPOSITION OF THE INNER SPHERE

The sequence of chemical and electrochemical stages in complicated electrode reactions depends primarily on the nature of the reactant complexes and may vary with

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[†] The slow exchange of electrons between cobalt(III) and cobalt(II) complexes of similar composition had earlier been attributed[119] to a considerable change in the cobalt–ligand bond length with change in the valency state of the cobalt. However, it was later established[120] that the difference in bond lengths between the hexammines is 0.15 Å, which differs little from other similar systems.

the experimental conditions, e.g. with change in the electrode potential. Thus nitrilotriacetate complexes of cadmium[139,140] and other metals[32] are directly reduced on a dropping mercury electrode at sufficiently negative potentials, but at more positive potentials the electrochemical stage of the cathodic process is preceded by detachment of an anion of nitrilotriacetic acid.

The occurrence of preceding chemical stages and their reversibility are usually assessed from the effect of the ligand concentration on the rate of the electrode reaction[4,32-35]. In order to diminish (or eliminate) the complicating influence of the diffuse structure of the electrical double layer such investigations are usually made at a high and constant solution concentration (ionic strength μ). In interpreting the order of the electrode reaction with respect to the ligand it is usually assumed that the equilibrium constants of the chemical stages remain unchanged over the range of ligand concentrations studied, but with a variable ionic strength or a considerable change in solution composition this requires special proof.

We shall first discuss reactions involving oxidised and reduced forms dissolved in the electrolyte, i.e. so called redox systems, and then the electrodeposition and the anodic dissolution of metals.

1. Redox Systems

Titanium(IV)–titanium(III) system

Irreversible cathodic and anodic waves are observed on charge transfer between titanium ions at a dropping mercury electrode in acid chloride[141-144], bromide[144,145], and sulphate[146] solutions. The dependence of the half-wave potential on the concentrations of hydrogen and chloride ions with $\mu = 1$ suggests[141-144] the electrochemical stage

$$\mathrm{Ti(OH)Cl^{2+} + e \rightleftarrows Ti(OH)Cl^{+}}, \tag{5}$$

the electrochemically active complexes in which are formed in preceding reversible chemical stages from the oxidised and reduced forms $Ti(OH)_2Cl_2$, $TiOCl^+$ and Ti^{3+} that predominate in solution. The sum of the transfer coefficients $\alpha' + \beta' = 1.00 \pm 0.05$ (where α' varies from 0.34 to 0.45). Charge transfer between titanium ions was studied[144,145] in 1 M HBr + KBr and in 0.06 M HBr + xM KBr (where $x = 0.02$–0.80), i.e. with a variable ionic strength in the latter case. It was concluded that the electrochemical stage involved the complexes $TiBr^{3+}$ and $TiBr^{2+}$, produced reversibly from the respective forms $Ti(OH)Br_2^+$ and Ti^{3+} that predominate in solution. The apparent transfer coefficients vary slightly with the solution composition, their sum being $\alpha' + \beta' \simeq 1.1$–$1.2$. In acid sulphate and sulphate–perchlorate electrolytes ($\mu = 1$)[146] the electrochemical stage involves the complexes $TiHSO_4^{3+}$ and $TiHSO_4^{2+}$, which are in equilibrium with the complexes $Ti(OH)HSO_4^{2+}$ and Ti^{3+} that predominate in solution.

Chromium(III)–chromium(II) system

The oxidation of labile hydrated Cr^{2+} ions at a mercury electrode is catalysed by halide and other anions, the catalytic effect diminishing in the sequence $I^- > Br^- > Cl^-$ [147,148], i.e. the sequence in which the specific adsorption of halide ions on mercury decreases. In the presence of sufficiently high chloride-ion concentrations the oxidation product is the inert complex $CrCl^{2+}$ [147-149]. In the presence of bromide ions inert complexes of Cr^{3+} and $CrBr^{2+}$ are formed, their concentration ratio depending on the electrode potential[148]. The composition of the reaction products, together with chronopotentiometric and other measurements, show that chloride and bromide ions adsorbed on mercury act as bridging ligands in the electrochemically active complexes $Hg\ldots X\ldots Cr^{II}$. The latter arise directly on the surface of the mercury electrode, not by the adsorption of CrX^+ complexes formed by a preceding homogeneous chemical reaction, as might be supposed[6]. The results show[148] that, in the oxidation of Cr^{2+}, chloride and bromide ions are non-bridging ligands which have a great influence on the kinetics of homogeneous electron-transfer reactions[150-158], in particular in the chromium(III)–(II) system[151,152,154-158]. Non-bridging ligands may influence the rate of electrochemical reactions[157].

An inner-sphere mechanism operates in the oxidation of Cr^{2+} on mercury in the presence of thiocyanate ions[159]. The inert $Cr(NCS)_i^{3-i}$ complexes contain 1–5 thiocyanate ions, the number increasing as the potential becomes more positive and with increase in the thiocyanate-ion concentration. The products *cis*-$Cr(NCS)_2^+$ and $Cr(NCS)_3$, formed when $CrNCS^+$ complexes are almost completely absent from the solution, indicate that polybridging electrochemically active complexes take part in the electrochemical stage. Here chromium ions are attached to nitrogen atoms in two or three thiocyanate ions, which in turn are attached to mercury through the sulphur atom. The chromium(III) complexes formed are adsorbed more strongly on the positively charged mercury surface than are thiocyanate ions. A detailed kinetic investigation of the electrochemical reduction on mercury of the inert complexes $Cr(NCS)_3.(H_2O)_3$ [160] and other similar chromium(III) complexes[161] included an independent study of the adsorption of the reactant complexes. Activity coefficients both of the predominant adsorbed complexes and of the transition state of the electrochemical stage must be taken into account in the kinetic equations[160].

Many processes involving the cathodic reduction of inert chromium(III) complexes have been studied[4,65], including subsequent chemical stages resulting in change in the composition of the inner sphere of the labile chromium(II) complexes formed[162-170].

Europium(III)–europium(II) system

Kinetic examination of the reduction of europium(III) at a mercury electrode in solutions of different concentrations of thiocyanate ions (mainly $\mu = 1$ with sodium perchlorate), allowing for the ψ_1 effect[54], indicates[8] comparable participation of Eu^{3+} and $EuNCS^{2+}$ ions in the cathodic process when present in comparable quantities in the solution. The $EuNCS^{2+}$ complex has a considerably larger standard heterogeneous rate constant than does the hydrated Eu^{3+} ion (respectively 8×10^{-4} and 4×10^{-5} cm s^{-1}). On passing from the bulk of the solution to that adjacent to the negatively charged electrode, however, the ratio $[Eu^{3+}]/[EuNCS^{2+}]$ increases. This is responsible for the comparable contributions by the two ions to the cathodic process, which had been disregarded hitherto[171]. Results[8,171] indicate an outer-sphere mechanism of the reduction of Eu^{3+} and $EuNCS^{2+}$. The latter complex loses the NCS^- ligand, probably after the electrochemical stage.

In the presence of excess of ethylenediaminetetra-acetic acid at pH 9.5 monoligand complexes $Eu^{III}L$ and $Eu^{II}L$ take part in the electrochemical stage, while $Eu^{III}L_2$ and $Eu^{II}L_2$ predominate in solution (where L is the anion of the complexone)[172].

Platinum(IV)-platinum(II) system

Steady-state polarisation and other measurements[173-185] indicate slowness of the electrochemical stage of charge transfer in PtX_6^{2-} and PtX_4^{2-} complexes (X = Cl, Br, I)[173-183,185] and other structurally similar complexes[181-184] at a platinum electrode. Study of the process in chloride complexes of platinum at platinum, rhodium, and iridium electrodes (0.4–1 M NaCl, 3 M H_2SO_4) suggested[176,180] that the electrochemical stage involved adsorbed complexes of the type $M\ldots Cl_{ads}\ldots PtCl_5^{3-}$ and $M\ldots Cl_{ads}\ldots PtCl_5^{-}$ (anodic and cathodic processes respectively), where M represents a metal atom on the electrode surface. It was assumed that the planar $PtCl_4^{2-}$ complex associates reversibly with a chloride ion adsorbed on the electrode and a free chloride ion, which bring its configuration to an octahedron[176,180]. An analogous mechanism was suggested[181] for the anodic oxidation of $Pt(NH_3)_4^{2+}$ in the presence of chloride and bromide ions, as well as for other platinum(II) complexes[177, 182-184]. It is consistent with the approximately first order of the oxidation of PtX_4^{2-} with respect to the ligand (Cl^-, Br^-) observed at high concentrations (~0.3–1 M) of chloride and bromide ions[174-177,180]. At low concentrations halide ions are subject to competition by water molecules, which is more successful with negatively charged platinum(II) complexes than with positively charged and neutral complexes of the type $PtX_{4-i}(NH_3)_i^{i-2}$, where X = Cl, NO_2 and $i = 2,4$.[181,182]

The oxidation of $PtCl_4^{2-}$ complexes on platinum has different mechanisms in the double-layer region of the charging curve and at more positive potentials, at which oxygen is adsorbed (1 M NaCl, 3 M H_2SO_4 [185,186]). On passing from potentials of 0.7–0.85 V (n.h.e.), at which chloride ions act as bridging ligands, to ~1.1–1.3 V the apparent transfer coefficient of the anodic process decreases from 0.9 to 0.48.[185] This is attributed[186] to a decrease in the effective negative charge of the adsorbed chloride ions, which stabilises electrons in d_{z_2} orbitals in adsorbed platinum(II) complexes, and these are transferred in the electrochemical stage. At ~1.1–1.3 V oxygen atoms (hydroxide ions) having a considerable negative charge appear owing to deprotonation of adsorbed water molecules on the platinum. This is probably responsible for their preferential involvement as inner-sphere bridges in the anodic oxidation of $PtCl_4^{2-}$ complexes. Hence the complexes $PtCl_4(H_2O)_2$ and $PtCl_6^{2-}$ (70% and 30%) have been detected by thin-layer voltammetry[179] among the products of the oxidation of $PtCl_4^{2-}$ complexes in 1 M hydrochloric acid at ~0.8–1.0 V. The change in state of water molecules adsorbed on platinum, on passing from the double-layer range to a more positive potential, is probably responsible for the similar change in mechanism of the anodic process in the $SbCl_6^-$–$SbCl_4^-$ [187] and arsenic(V)–(III) [188] systems.

The inhibiting effect of the ligand X on the cathodic reduction of PtX_6^{2-} complexes (X = Cl, Br) on platinum is attributed[176,185] to a preceding reversible heterogeneous chemical reaction

$$M-X+PtX_6^{2-}\rightleftarrows M\ldots X\ldots PtX_5^{-}+X^{-}, \qquad (6)$$

which may occur by an exchange type of mechanism. The surface complex formed by reaction (6) takes part in a slow electrochemical stage. The closely similar transfer coefficients for cathodic and anodic processes in the $PtCl_6^{2-}$–$PtCl_4^{2-}$ [174-176] and $PtBr_6^{2-}$–$PtBr_4^{2-}$ [177] systems, whose sum in the double-layer potential range of the platinum electrode is ~2, indicate simultaneous or almost simultaneous transfer of two electrons in the electrochemical stage. A similar mechanism had been suggested earlier[189-193] for the transfer of electrons between octahedral platinum(IV) and planar platinum(II) complexes in the bulk of the solution.

The great instability of platinum(III) complexes is indicated by the simultaneous transfer of two electrons from chromium to platinum via a bridging inner-sphere chloride ion when quadrivalent platinum complexes $PtCl(NH_3)_5^{3+}$ are reduced by Cr^{2+} ions[194,195]. The unstable quadrivalent chromium complex formed, $CrCl^{3+}$, is then reduced by bivalent chromium. The hypothesis of a successive transfer of electrons in electrode reactions of platinum(IV) and platinum(II) complexes[173,183,184] therefore requires further support. The lack of influence of chloride ions (at concentrations of 0.3–1 M) on the rate of electrochemical reduction of $PtCl_6^{2-}$ and the small apparent transfer coefficient of the cathodic process (0.44) suggest that the mechanism of the reduction of $PtCl_6^{2-}$ complexes[183] differed from that suggested[176,180], perhaps owing to different surface states of the platinum electrodes. The effect of the chemisorption of foreign species on the kinetics of electrode reactions of platinum complexes has been investigated[184].

Other systems

The cathodic reduction of inert cobalt(III) and rhodium(III) complexes[4,64-66,169,196,197], like that of chromium(III) complexes, usually involves subsequent chemical stages leading to rearrangement of the resulting labile complexes of the reduced forms. Reversible chemical stages have recently been established[198], as a result of which the forms of bi- and tervalent iron predominating in acetate solution are converted into their acetate complexes, and these take part directly in the slow electrochemical stage on a platinum electrode. During charge transfer between ferrous and ferric ions at a platinum electrode in the presence of salicylate ions (0.01–0.1 M) and an acetate buffer the electrochemical stage involves $FeSal^+$ and FeSal complexes formed by preceding reversible chemical reactions from the oxidised and reduced species $FeSal_2^-$ and Fe^{2+}, which predominate in solution[199].

2. Electrodeposition and Anodic Dissolution of Metals

The electrodeposition and the anodic dissolution of metals in complexing solutions, as in non-complex media[40-43,200], may involve successive electrochemical stages. We shall consider initially the simpler one- and two-electron electrode reactions, which include a single electrochemical stage uncomplicated by crystal growth or disintegration. Gerischer[60] regarded such processes, occurring on the surface of metal amalgams, as macromolecular reactions of the type

$$M^{(z)}X_k+ze\rightleftarrows M+kX, \qquad (7)$$

where $M^{(z)}X_k$ is a complex directly involved in the electrochemical stage. With $k > 1$, however, a single-stage mechanism is improbable for reaction (7) [32,33]. A similar structure must be expected for the activated complexes of the single electrochemical stage of cathodic and anodic processes[52]. In view of this and the fact that the stage of ionisation of metal atoms is preceded by formation of their complexes on the electrode surface (adsorption of ligands)[201-203] the anodic reaction occurring on the electrode can be represented[204] by the sequence of stages

$$\mathrm{E{-}M^{(0)}} + k\mathrm{X} \rightleftarrows \mathrm{E{-}M^{(0)}X}_k\,, \tag{8.1}$$

$$\mathrm{E{-}M^{(0)}X}_k \rightleftarrows \mathrm{E{-}M^{(z)}X}_k + z\mathrm{e}, \tag{8.2}$$

$$\mathrm{E{-}M^{(z)}X}_k + (n-k)\mathrm{X} \rightleftarrows \mathrm{E} + \mathrm{M^{(z)}X}_n, \tag{8.3}$$

where E is the electrode to which are directly bound the ionising, formally "zero-charged" metal atoms and their complexes $M^{(0)}$ and $M^{(0)}X_k$. The adsorption of ligands and complexes is accompanied by displacement of water molecules or other species adsorbed on the electrode, which for simplicity is ignored in Eqns. (8.1)–(8.3). The concentration of the metal complex $M^{(z)}X_n$ predominating in the solution will be regarded as identical with the total concentration of metal ions in the solution.

If anodic and cathodic processes involve the same stages (8.1)–(8.3), slow occurrence of the electrochemical stage (8.2) and reversibility of the chemical stages (8.1) and (8.3) should lead to satisfaction of the equation[204]

$$\left|\partial\lg\frac{i}{i_{d,c}-i}\Big/\partial\lg[\mathrm{X}]\right|_{(\varphi-\varphi_0)<0} + \left|\partial\lg\frac{i}{i_{d,a}-i}\Big/\partial\lg[\mathrm{X}]\right|_{(\varphi-\varphi_0)>0} = n, \tag{9}$$

where i is the polarising current density at the electrode potential φ, with $i_{d,c}$ and $i_{d,a}$ the limiting diffusion currents of cathodic and anodic processes respectively, and φ_0 is the equilibrium potential of the $M/M^{(z)}X_n$ system. It is assumed that $[X] \gg [M^{(z)}X_n]$ and that the coverage of the electrode surface by electrochemically active complexes is insignificant. Relation (9) should be satisfied independently of whether the equilibrium constants β_{0k} and β_{kn} of the heterogeneous chemical stages (8.1) and (8.3) are functions of the electrode potential. If the dependence of these constants on φ can be neglected, the relation

$$\left|\partial\lg\frac{i}{i_{d,c}-i}\Big/\partial\varphi\right|_{(\varphi-\varphi_0)<0} + \left|\partial\lg\frac{i}{i_{d,a}-i}\Big/\partial\varphi\right|_{(\varphi-\varphi_0)>0} = \frac{zF}{2{,}3RT} \tag{10}$$

should also be satisfied, since with a single electrochemical stage the sum of the apparent transfer coefficients is equal to the total number of electrons transferred[40-42].

Formulae (9) and (10) can conveniently be used as criteria in study of the mechanism of the electrodeposition and the anodic dissolution of metals in complex electrolytes. Since the electrochemically active complexes in the ionisation of metal atoms contain metal–metal bonds, the opposite cathodic process should correspond to a transition state of similar structure, in conformity with the mechanism (8.1)–(8.3). Examination of published data shows that relation (9) is satisfied more often than is (10). A probable reason is the dependence of the equilibrium constants of reactions (8.1) and (8.3) on the electrode potential[204], which may be due in particular to variation in the ψ_1 potential.

Table 3 lists parameters of electrode reactions in which, in conformity with the mechanism (8.1–8.3), integral or nearly integral orders‡ are observed with respect to the ligand in cathodic and anodic processes, and formula (9) holds. The satisfaction of relations (9) and (10) in the first four systems in Table 3 supports the mechanism (8.1)–(8.3), which includes the inner-sphere electrochemical stage (8.2). Variation of the electrode potential either has no effect on the concentration of electrochemically active complexes or has opposite effects on the slopes of cathodic and anodic Tafel lines in these systems, and such effects balance out.

Table 3. Parameters (at 25°C) of electrode reactions for which Eqn. (9) is satisfied*

System	Complexes in soln.	k	α'	β'	Ref.
Zn(Hg)/Zn(II), $P_2O_7^{4-}$	$Zn(P_2O_7)_2^{6-}$	1	0.62	1.26	205
Zn(Hg)/Zn(II), NH_3; $\Delta\varphi \lesssim 50$ mV	$Zn(NH_3)_i^{2+}$, $i=3,4$	2	1.10	0.80	206
Pb(Hg)/Pb(II), $P_2O_7^{4-}$	$Pb(P_2O_7)_2^{6-}$	1	0.80	1.18–1.28	207
Au/Au(I), CN^-	$Au(CN)_2^-$	1	0.50	0.45	210, 211
Pd/Pd(II), Cl^-	$PdCl_4^{2-}$	2	0.84	0.84	208
Pd/Pd(II), Br^-	$PdBr_4^{2-}$	2	0.82	0.82	209

*k = number of ligands in electrochemically active complex; α' and β' are the apparent transfer coefficients of cathodic and anodic processes.

The dependence of the exchange current density measured near the equilibrium potential of amalgams of zinc[60], cadmium, and other metals[33,34] on the concentration of the complexes and the species forming them is also consistent with the mechanism (8.1)–(8.3).

The proportionality between the rate of cathodic reduction of the complexes $PdCl_4^{2-}$ [208,212-214] and $PdBr_4^{2-}$ [209,212,215] and their concentration, established with palladium[208,209,214] and dropping mercury§ electrodes[212,213,215], indicates that the electrode surface is only slightly covered by the reducible complexes.

A second order with respect to the chloride ion had been observed earlier for the anodic ionisation of palladium[216,217]. Nearly integral values (–2) of the order with respect to the ligand are observed for the cathodic reduction of PdX_4^{2-} (where X = Cl [208,213], Br [209,215,218]) at palladium and dropping mercury electrodes. Complexes of $PdCl_2$ are considered[219,220] to undergo direct reduction in the electrodeposition of palladium.

The sum of the apparent transfer coefficients $\alpha' + \beta'$ for the Pd/Pd^{II} system is slightly <2 (Table 3), which, on the hypothesis of the simultaneous involvement of two electrons in the slow electrochemical stage, can be attributed to a decrease in the concentration of electrochemically active complexes with increase in the polarisation of the electrode. Thus increase in the positive potential of a palladium anode may be accompanied by a decrease in the concentration of surface PdX_2^{2-} complexes owing to displacement of their X^- ligands by water molecules[204]. The coefficient α' determined from the Tafel relationship may be underestimated because of a breakdown of equilibrium in the preceding chemical stage.

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‡The kinetic order departs considerably from an integral value for the ionisation of zinc from its amalgam in a pyrophosphate electrolyte (the order of the anodic process with respect to $P_2O_7^{4-}$ is 0.76 at –1.28 V s.c.e.). The corresponding value $\beta' = 1.26$ (Table 3) was obtained with $[P_2O_7^{4-}] = 0.025$ M. [205]

§At $PdCl_4^{2-}$ and $PdBr_4^{2-}$ concentrations $\gtrsim 2 \times 10^{-4}$ M their reduction at a dropping mercury electrode is inhibited by the reduction products, which accumulate on the mercury drop during its lifetime[212,213,215].

The slow occurrence of this stage in the cathodic reduction of $PdCl_4^{2-}$ complexes on a palladium electrode with a high concentration of chloride ions is indicated by a decrease in the product $i\tau^{\frac{1}{2}}$ with increase in the polarising current density i (where τ is the transition time)[221]. Detachment of a chloride ion from the complex $PdCl_4^{2-}$ is the slow stage, for which application of a galvanostatic method[221] gave the rate constant as 500 s^{-1} (for 0.06–1 M HCl and 3 M H_2SO_4 at 25°C). Smaller values of k^- (in s^{-1} at 25°C)—8.9 ± 0.8 (in 0.5 M $HClO_4$ by a spectrophotometric method)[222] and 5.6 ± 0.5 [in 0.3 M $(Li, H)ClO_4$ by the temperature-jump method][251]—have been found for the homogeneous aquation

$$PdCl_4^{2-} + H_2O \xrightarrow{k^-} PdCl_3H_2O^- + Cl^- . \qquad (11)$$

This discrepancy may be due to a catalytic effect of the surface of the palladium electrode on the rate of dissociation of chloride complexes of palladium. Since it has been concluded[221] that the preceding chemical stage has a homogeneous character, this problem requires further investigation.

The diffusion nature of the limiting currents observed in the reduction of $PdCl_4^{2-}$ complexes at a dropping mercury electrode suggests[213] that the preceding chemical reaction may be catalysed by mercury ions or atoms. The rate of cathodic reduction of $PdCl_4^{2-}$ and $PdBr_4^{2-}$ complexes increases sharply on passing to a palladium electrode, which indicates an inner-sphere mechanism of the electrochemical stage. It probably involves complexes, adsorbed on the electrode surface, which contain two halide ions and palladium atoms directly attached to metal atoms on the electrode surface[213,215], which is consistent with the mechanism (8.1)–(8.3).

The participation of two electrons in the slow electrochemical stage of the reduction of $Pd\,py_4^{2+}$, $Pd(NH_3)_4^{2+}$, and $Pd\,en_2^{2+}$ complexes (py = pyridine) was deduced from an analysis of non-stationary galvanostatic curves[223]. The apparent transfer coefficient of the cathodic process was determined[223] to be respectively 0.91, 0.85, and 1.46 for these complexes, and the absence of preceding slow chemical stages was established. Oscillopolarographic oxidation of the reduction products of $Pd(CN)_4^{2-}$ complexes at a mercury cathode reveals intermediate complexes of univalent and zerovalent palladium[224], probably stabilised by cyanide ions. A similar situation is found in the cathodic reduction of cyanide complexes of cobalt(II)[225] and nickel(II)[226], as well as other similar complexes formed by strong-field ligands[4]. Yet the Tafel slopes corresponding to the reduction on mercury of ammine (ammonia is a weak-field ligand) nickel(II) complexes (42 mV[227] and 60 mV[228]) indicate the simultaneous transfer of two electrons in the electrochemical stage. The latter involves $Ni(NH_3)_2^{2+}$ complexes formed by a rapid chemical reaction from higher ammine complexes, which supports the mechanism (8.1)–(8.3).

The kinetic parameters determined[207,229–231] in a study of irreversible cathodic and anodic processes for the $Zn(Hg)/Zn(OH)_4^{2-}$ system, in contrast to the systems listed in Table 3, conform neither to Eqn. (9) nor to (10). This is explained[229,230] by differences in the nature of the electrochemical stages of cathodic and anodic processes. The approximate orders of −2 and 1 with respect to hydroxide ions for the two processes suggest that the complexes $Zn(OH)_2$ and $ZnOH^-$ are involved in their slow electrochemical stages. Near the equilibrium potential of the system the anodic process is of second order with respect to hydroxide ions[60]. An approximate halving of the order for the ionisation of zinc atoms with respect to the ligand on passing from low to high anodic polarisations is observed also when zinc amalgam dissolves in the presence of ammonia molecules[206] and for zinc in a citrate electrolyte[232]. This is probably due to competition with the adsorbed ligands by water molecules, a considerable proportion of which, at the low negative surface charges on the electrode characteristic of high anodic polarisations, are oriented with the oxygen atoms towards the surface zinc atoms, which should decrease the concentration of electrochemically active complexes and the order of the anodic process with respect to the ligand. The approximate halving of the apparent transfer coefficient of the anodic process which accompanies[206,232] the decrease in order with respect to the ligand may be due to a transition from a slow two-electron stage to a one-electron stage. The apparent transfer coefficients of cathodic and anodic processes (0.82 and 0.34) found for the $Zn(Hg)/Zn(OH)_4^{2-}$ system in 4 M K(OH, F) solution¶ are attributed[231] to a stepwise transfer of electrons in cathodic and anodic processes. However, these values are consistent also with a two-electron electrochemical stage during cathodic polarisation and slow detachment of the first electron at high anodic polarisations. It has been concluded that intermediate univalent zinc species are adsorbed on zinc during its electrodeposition and anodic dissolution in the presence of malonate ions (pH 6–7)[233] and in alkaline solutions[234,235].

Consecutive transfer of electrons probably always occurs in three-electron reactions, whose stage-by-stage mechanism has been studied in detail on the $Bi(Hg)/Bi^{III}$ and $In(Hg)/In^{III}$ systems[41–43,200]. The kinetics and the mechanism of the anodic dissolution of indium in various media have been surveyed[200]. The cathodic reduction of indium(III) complexes is complicated by slow chemical stages and also by the dependence of the concentration of adsorbed complexes and ligands on the electrode potential (see reviews[38,200,236]), which adds to the difficulty of determining the kinetic parameters of the cathodic process and of subsequent analysis based on Eqns. (9) and (10).

The three-electron cathodic reduction of rhodium(III) complexes also involves one- or two-electron stages[223,237–241]. With $RhCl_6^{3-}$ and $RhCl_5H_2O^{2-}$ complexes on mercury[238,241] and rhodium[240] electrodes the slow electrochemical stage is preceded by reversible detachment of some of the chloride ions from the initial complexes. The rapid replacement of inner-sphere ligands in inert complexes may be due to catalysis by the electrode surface or intermediate products. Heterogeneous catalysis of the replacement of ligands in inert complexes has been studied[242] on cobalt(III) complexes.

The bond between electrochemically active complexes and the electrode may vary significantly in character for different electrochemical stages of the same many-electron reaction. According to the above considerations the last electrochemical stage of electrodeposition, with formation of metal atoms (their surface complexes), should have a non-bridging inner-sphere mechanism, which occurs e.g. in the sequence of stages (8.3), (8.2), and (8.1). In the case of the initial electrochemical stages of electrodeposition, as a result of which intermediate uni- or bi-valent metal complexes are formed from the initial complexes, an outer-sphere or a bridging inner-sphere

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¶Apparent transfer coefficients $\alpha' = 0.80$ and $\beta' = 0.52$ were determined[207] by a potentiodynamic method for the $Zn(Hg)/Zn(OH)_4^{2-}$ system in 3 M (KOH + NaCl) solution.

mechanism may operate†. The presence of bridging ligands in bivalent zinc, cadmium, and lead complexes adsorbed on a mercury electrode[243-246] (see also references in Refs. 247 and 248) does not exclude a non-bridging inner-sphere mechanism of the electrochemical stage in the reduction of these complexes. Complexes adsorbed through the ligand, which predominate on the electrode surface, may be converted by a preceding rapid chemical reaction into electrochemically active complexes containing a metal–metal bond.

It follows from the above considerations that, with a slow electrochemical stage complicated by complex formation, the main features of the electrochemical kinetics are the same on liquid and solid electrodes. The kinetics of practically important processes of the electrodeposition of solid metals from complex electrolytes have been examined in a monograph[249]. A review has recently been published[250] on the electrodeposition of noble metals.

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A very important but little studied problem is the relation between the kinetic parameters of an electrode reaction and the electronic structure of the complexes. The electrode reactions discussed above involved the transfer of electrons from the electrode to orbitals localised mainly on the metal ion or in the reverse direction[4]. The transfer of t_{2g} electrons from or to low-lying orbitals of a metal occurs more rapidly than that of e_g electrons[252,253]. This is explained by the greater change in metal–ligand bond length in the latter case, and hence the greater energy of rearrangement of the inner coordination sphere (while its composition remains unchanged).

In the electrochemical reduction of complexes electrons may be transferred also to orbitals of inner-sphere ligands. In order to elucidate the reaction mechanism in such cases it is necessary to make a parallel kinetic study of the cathodic reduction of coordinated and free ligands[254-257].

The kinetic investigations on electrode reactions of trisbipyridyl and similar complexes of iron in water and dimethylformamide[258] and of trisbipyridyl complexes of ruthenium, osmium, chromium, titanium, vanadium, and molybdenum in dimethylformamide[254-256] have revealed two groups of electrode reactions. One group of complexes, with which a t_{2g} electron is transferred, have rate constants $k_S = 0.8–1.3$ cm s^{-1}. The other group of complexes, with which an electron localised on a π^* orbital of a ligand is transferred, correspond to $k_S = 0.1–0.3$ cm s^{-1}. The fact that k_S is relatively unaffected by the nature of the electrode (mercury, platinum), the solvent (water, dimethylformamide), the state of oxidation of the metal, or the charge on the complex indicates the decisive role of rearrangement of the inner coordination sphere in determining the rate of the electrochemical stage[256]. Electron transfer to orbitals of the ligand is suggested in the second group of complexes by the closeness of their k_S values to those found for the bipy/bipy$^-$ system (0.13 and 0.21 cm s^{-1} for mercury and platinum electrodes respectively). The redox properties of ligands coordinated by metal ions has recently been studied intensively. This topic is of intrinsic interest, and will not be considered here.

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† With a bridging inner-sphere mechanism one or more inner-sphere ligands of the electrochemically active complex are attached directly to metal atoms on the electrode surface. In both heterogeneous and homogeneous electron-transfer reactions bridging ligands may fill various functions[5].

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Polarography of Organoelementary Compounds of Non-transition Elements

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The electrochemical behaviour of many organoelementary derivatives containing a non-transition element is described. The mechanism of the electrode processes and the effect of the conditions of electrolysis are reviewed, mainly at a dropping mercury electrode. A list of 156 references is included.

CONTENTS

Although polarography is used fairly widely in the study of organoelementary compounds, published data have not yet been collected together. The present Review attempts to summarise and systematise very briefly the results of numerous investigations on derivatives of non-transition elements.

I. ORGANOMERCURY COMPOUNDS

These compounds are of especial interest for polarography, since they can be formed by the reaction of mercury with certain depolarisers (e.g. halogeno-derivatives, sulphur-containing compounds, certain aldehydes and ketones), as well as intermediate and final products of electrode processes, e.g. in the reduction of iodonium salts[1]. If sufficiently rapid, the formation of organomercury compounds changes substantially the character and the mechanism of the electrode process, which must therefore always be borne in mind in the study of electrode processes.

The first detailed studies of the behaviour of arylmercuric salts RHgX [2,3] revealed the presence of two one-electron waves on the polarograms in 50% aqueous-ethanolic solutions, with the half-wave potential of the first wave appreciably affected by the nature of the anion X^-.[2,4] Organomercury salts are able to dissociate[5,6]:

$$\mathrm{RHgX} \overset{K_1}{\rightleftarrows} \mathrm{RHg}^+ + \mathrm{X}^- \ . \qquad (1)$$

If an electrolyte containing a common anion X^- is present in solution, complexes are formed:

$$\mathrm{RHgX} + \mathrm{X}^- \overset{K_2}{\rightleftarrows} \mathrm{RHgX}_2^- . \qquad (2)$$

Reduction of the cation RHg^+ is reversible[4]:

$$\mathrm{RHg}^+ + e \rightleftarrows \mathrm{RHg}^{\cdot} . \qquad (3)$$

The resulting radical $RHg\cdot$ dimerises to give an extremely unstable "organic calomel" R_2Hg_2. Formation of the latter was suggested[7,8] after comprehensive discussion of the possibilities for the cathodic reduction of organomercury salts. It has been proved by chronopotentiometric investigations[9], in particular establishment of the nature of the products of interaction of organomercury salts and their reaction with metallic mercury, and of interaction between various disubstituted mercury derivatives[10,11], as well as study of the products of the simultaneous reduction of two different organomercury salts and of reduction of a salt on an electrode covered with the adsorbed symmetrical organomercury compound[10-12].

The organic calomel is converted by disproportionation (which is probably reversible[10,13]) fairly rapidly into the symmetrical organomercury compound:

$$\mathrm{R_2Hg_2} \rightleftarrows \mathrm{R_2Hg} + \mathrm{Hg} \ . \qquad (4)$$

It is reduced irreversibly at the electrode[2,10,14-16]:

$$\mathrm{R_2Hg_2} + 2e + 2\mathrm{H}^+ \rightarrow 2\mathrm{RH} + 2\mathrm{Hg}, \qquad (5)$$

corresponding to the second wave on the polarograms of organomercury salts.

Another possibility is that an organic calomel may be formed by a so called "electrochemical desorption mechanism", in which a radical formed at the electrode reacts with the initial substance and simultaneously acquires a second electron from the electrode, as well as, though less probably, by a "hydride" mechanism, in which the product RHg^- of the addition of two electrons to the initial organomercury cation at the potential of the first wave reacts with the initial cation RHg^+.[13]

The lifetime of the organic calomel R_2Hg_2 (before its disproportionation by reaction 4) decreases according to the nature of R in the sequence[12]
$C_2H_5 >$ cyclo-$C_5H_9 >$ n-$C_3H_7 >$ iso-$C_3H_7 \simeq$ n-$C_5H_{11} \gg$ 2,4,6-$(CH_3)_3C_6H_2 >$ 2-$C_{10}H_7 > C_6H_5 \gg CH_2:CH$
It has been established[13] that neither the organic calomel $(RHg)_2$ nor the unsymmetrical calomel ArHgHgAlk is able to dissociate into free radicals.

The reversible character of transfer of the first electron and the accompanying chemical reactions are responsible for the form of the first wave and the influence of various factors on its parameters[4,15]. Thus if X is not a halogen, the wave in the absence of halide ions in solution is described[4] by the equation for a reversible one-electron process followed by rapid bimolecular interaction of the electrode products in the adjacent layer of solution[16]:

$$E = \varepsilon_0 - \frac{RT}{nF} \ln \frac{i^{2/3}}{i_d - i}, \tag{6}$$

where ϵ_0 is the so called characteristic potential, independent of concentration[16].

When RHgX, where X is a halogen, undergoes reduction in the absence of halide ions in solution, such ions appear at the electrode surface as a result of the electrode process (1), their concentration being greater the stronger the current. The resulting halide ions undergo reaction (2) with the initial salt RHgX, which makes the potential more negative, as occurs with bulk catalytic waves in unbuffered media, when hydroxide ions are formed provided that the wave height is still proportional to the catalyst concentration[16]. In both these cases the wave form is described by the formula

$$E = \text{const} - \frac{RT}{F} \ln K_2 - \frac{RT}{F} \ln \frac{i^{5/3}}{i_{\text{lim}} - i},$$

where a tenfold increase in the depolariser concentration makes the half-wave potential more negative by 40 mV.

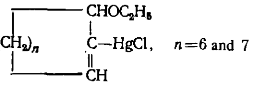
The form of the polarographic wave obtained for an organomercury halide in a solution containing excess of this halide ion is described by Eqn. (6), owing to the occurrence of reaction (2), as with bulk catalytic waves in buffered solutions. The quantity ϵ_0 becomes more negative with increase in the concentration of halogen in the solution[4]. For the ethylmercury halides the half-wave potential of the first wave becomes more negative in the sequence of derivatives Cl → Br → I.

The half-wave potential of the first reversible reduction wave of pyrid-3-ylmercuric acetate becomes less negative with lengthening of the drop period of the electrode and with increase in the depolariser concentration[15], in conformity with the Koutecký–Hanuš theory[17] for a reversible process followed by rapid dimerisation of the electrode products. In just the same way, in agreement with the theory[18] of irreversible electrode processes, for which the rate of electron transfer competes with a bimolecular reaction of the species involved in the electrochemical reaction, the half-wave potential of the second wave becomes more negative with increase in the depolariser concentration[15]. However, organomercury salts exhibit an additional shift in the half-wave potential, due to inhibition of the process by adsorbed reaction products.

The nature of the radical R influences the ease of reduction, the characteristic potential ϵ_0 (or the half-wave potential) becoming less negative with decrease in the acidity pK_a of the corresponding hydrocarbon RH.[19] However, there is no linear relation between these quantities. Negative values of ϵ_0 for the first wave of organomercury perchlorates with 0.1 N tetraethylammonium perchlorate as supporting electrolyte in dimethylformamide at 25°C are 0.612, 0.594, 0.613, 0.535, 0.544, and 0.370 V (s.c.e.) when R represents respectively methyl, ethyl, n-propyl, n-pentyl, phenyl, and benzyl[19].

With derivatives of phenylmercury salts not only cations of the initial compounds but also free radicals formed by electron transfer to them are adsorbed on the electrode[20]. Dimerisation of the radicals is then a surface process: i.e. the radicals undergo dimerisation when adsorbed on the electrode. The wave is then described not by Eqn. (6) but by the corresponding expression containing the square root of the current in the numerator of the antilogarithm[21]. Rate constants of surface dimerisation (or those of formation of the symmetrical compound, for it is assumed[20] that formation of an organic calomel is a very rapid reversible process, followed by the slower direct reaction (4) of the free radicals of phenylmercury and several of their derivatives with substituents in the benzene ring have been determined[20] by voltammetry with a linearly varying potential and reversal of the current. The rate constant for free phenylmercury radicals at 25°C is ~ 10^{13} cm^2 s^{-1} mole^{-1}. The rate of dimerisation increases or decreases on the introduction of electron-donating or electron-accepting substituents into the benzene ring, with a satisfactory correlation between the logarithm of the rate constant and the σ-parameter of the substituent[20].

cis-1-Chloromercuri-9-ethoxycyclononene and *cis*-1-chloromercuri-10-ethoxycyclodecene. When the group R in an organomercury salt RHgX is very large, the rate of dimerisation of the free radical RHg· is so slow that it ceases to influence the polarographic characteristics of the waves. This situation is probably present[22] in the reduction of these two compounds



$$(\text{CH}_2)_n\text{—CHOC}_2\text{H}_5\text{—C(HgCl)=CH—},\quad n=6 \text{ and } 7$$

which in 50% aqueous dioxan each give two waves, representing reduction to the free radical and its further reduction with separation of metallic mercury. The first wave is reversible, its form being described by the usual Heyrovský–Ilkovič equation for reversible waves with one transferable electron; its half-wave potential is independent of the concentration of depolariser in the solution, and both factors indicate absence of rapid dimerisation of the radicals. When a solution of these compounds in dimethylformamide is electrolysed at the temperature of liquid nitrogen, it acquires a deep yellow colour, which remains for a long time; when the solution warms up to room temperature, however, the colour characteristic of the free radicals disappears after a few minutes[22]. This is also an indication of the comparative stability of the radicals. The second wave on polarograms of these compounds is irreversible, its half-wave potential becoming more negative with increase in the depolariser concentration. For both waves these potentials depend on the pH. Although the investigators[22] speak of the diffusion nature of both waves, the first wave is appreciably lower than the second ($i_{\text{lim}}'/i_{\text{lim}}'' \simeq 2/3$) and has a comparatively high temperature coefficient (increasing from 2.2 to 3.8% deg^{-1} with rise in temperature from 21 to 42°C). The first wave probably has partly kinetic restriction.

trans-1-Chloromercuri-11-methoxycycloundecene and *trans*-1-chloromercuri-13-methoxycyclotridecene. These compounds have been studied under the same conditions[23] (n = 8 and 10 in the above general formula, with the ethoxy-group replaced by methoxyl). They each give two one-electron waves, whose limiting currents are independent of pH, while the half-wave potentials vary with pH. The first wave is reversible, and the second irreversible; free radicals appear in the first stage, and either dimerise or acquire a second electron, eliminate mercury, and form an unsaturated compound. The change from *cis*- to *trans*-isomers and the increase in size of the ring result in less negative half-wave potentials of both waves[23]. These potentials for the first waves of ring-substituted bromomercuriphenyl acetates do not correlate with the Hammett σ-constants[24]. Such correlation between the half-wave potentials of the first waves and the nature of the substituents is absent also from other α-oxomercuric halides[24].

Fluorinated aliphatic organomercury salts. These give two waves representing reduction of the carbon–mercury bond, but in some cases more than two electrons are involved, probably owing to electrochemical cleavage of a carbon–fluorine bond[14].

Perfluorophenylmercuric bromide. In 30% aqueous methanol with 1 M sodium perchlorate as supporting electrolyte this fluorinated compound gives two waves having half-wave potentials (with a depolariser concentration of 2×10^{-4} M) of respectively −0.02 and −0.31 V (relative to an aqueous saturated calomel electrode). It has been shown galvanostatically that the first stage of reduction gives perfluorodiphenylmercury, which is able to form up to ten adsorbed layers on the electrode[25].

Pyrid-3-ylmercury chloride and acetate. In buffered aqueous solutions each of these compounds gives two one-electron diffusion reduction waves (the first of which is reversible), whose half-wave potentials become more negative at pH > 5.0 (at pH 4 these potentials are respectively 0 and −0.37 V independently of the nature of the anion). The waves are distorted by adsorption of the reaction products, so that hysteresis is observed on the polarograms[15].

2-Piperidinoethylmercuric and 2-diethylaminoethylmercuric chlorides. These compounds are reduced in two one-electron stages (whose half-wave potentials in 50% aqueous ethanol are −0.345 and −0.70 V for the former chloride, and −0.35 and −0.62 V for the latter); these potentials are appreciably more negative in dimethylformamide[26]. The reduction products are a symmetrically disubstituted mercury derivative in the first stage, and a secondary amine (piperidine or diethylamine) and ethylene in the second stage. Only traces of tertiary amines were detected among the products of electrolysis[26].

Thien-2-ylmercuric chloride. In buffered solutions this compound gives two one-electron waves (at pH < 8 the first wave is concealed by the anodic mercury-dissolution current).[15] The half-wave potentials become more negative with increase in pH; at pH > 9 that of the second wave ceases to depend on pH, its value then being $E_{\frac{1}{2}} = -0.86$ V (s.c.e.). The first wave is reversible in character, and its half-wave potential is influenced by subsequent dimerisation of the electrode products.

5-Acetylthien-2-ylmercuric bromide. In a 30% aqueous dimethylformamide solution of 1 M sodium perchlorate this compound gives three reduction waves, of which the first two (half-wave potentials −0.06 and −0.73 V s.c.e.) are one-electron diffusion waves corresponding to reduction of the organomercury moiety, and the third represents reduction of the keto-group in the acetylthiophen formed by the first two processes[27]. Galvanostatic study of the bromide shows that it forms adsorbed multilayers on the surface of the mercury electrode.

2-Methoxyethylmercuric salts. Products of the addition of mercury(II) salts to alkenes in methanol, of the type $CH_3O.CHR.CH_2.HgX$ (where X is an acid radical), behave similarly to other organomercuric salts when polarographed: they give two reduction waves on the polarograms, the first of which is reversible and corresponds to formation of the radical R′Hg· adsorbed on the mercury (its half-wave potential does not depend on the pH but is affected by the nature of the anion); the second wave is an irreversible reduction of the radical (or "calomel") to R′H with the liberation of Hg^0.[28]

2-Hydroxyethylmercuric salts. In neutral or alkaline buffered solutions these compounds HOC_2H_4HgX give two pH-independent one-electron diffusion waves with half-wave potentials of −0.45 and −1.10 V for the chloride, and −0.63 and −1.30 V for the acetate. On acidification of the solutions the height of the first wave increases at the expense of the second, so that at pH < 5 a single two-electron wave remains[29]. Preparative electrolysis at potentials corresponding to the first wave give the symmetrical bishydroxyethylmercury[30]. At those of the second wave ethanol and ethylene are formed, the proportion of the alcohol increasing when the solution is made alkaline; in acid solutions, however, the yield of ethylene approaches 100%.[29] The formation of ethanol may be due to reduction of the symmetrical bishydroxyethylmercury formed on electrolysis[30].

2-Chloromercuri-3,3,3-trifluoropropan-1-ol. In a solution of 0.1 *N* potassium chloride in 80% ethanol this compound and its ethers $CF_3CH(HgCl)CH_2OR$ give two one-electron diffusion waves (with half-wave potentials of −0.37 and −0.080 V (s.c.e.) for the propanol). On acidification the first wave grows at the expense of the second, so that in acid medium only a single wave appears with $E_{\frac{1}{2}} = -0.37$ V.[31] Electrolysis in acid medium at the potential of the first wave entails protonation of the intermediate radical with further transfer of a second electron, as a result of which the ether bond is ruptured and the alkene $CF_3CH:CH_2$ is formed. At the potential of the second wave in neutral or alkaline media carbon–mercury and carbon–fluorine bonds are broken with formation of difluoroallyl alcohol (or an ether $CF_2:CHCH_2OR$).[31]

o-Chloromercuriphenol. The usual two one-electron diffusion waves are observed in buffered aqueous solutions. With a buffer containing nitric acid (0.05 M HNO_3 + 0.45 M $NaNO_3$), however, waves of unusual character are observed owing to the very sparing solubility of the intermediate formed on the electrode by transfer of the first electron[32]: the half-wave potential of the first wave becomes more negative with increase in the depolariser concentration, owing to retardation of the process by a reaction product; and in the second wave the current in the lower part is independent of the depolariser concentration, whereas the upper part of the wave is almost rectangular, the ascending portion of the wave passing abruptly, at an angle, into a limiting-current plateau. The absence of dependence of the current in the lower part of the wave on the concentration of the starting material is attributed[33,34] to a constant surface concentration of the reactant, due to its great adsorbability and very low solubility. The equations deduced[32] for both waves and the dependence of the half-wave potential of the first wave on the depolariser concentration reproduce correctly the peculiarities of the reduction waves for *o*-chloromercuriphenol in aqueous nitric acid.

Ferrocenylmercury salts. Both these compounds and mercury salts of manganese and rhenium cyclopentadienyltricarbonyls are reduced similarly to ordinary organomercury salts[35]. However, here two-step reduction waves (with respect to mercury), each corresponding to the transfer of one electron, can be obtained only in a 0.1 M solution of tetraethylammonium perchlorate in 90% dioxan (under these conditions neither ferrocene nor the manganese and rhenium atoms in the above compounds are involved in the electrode process). In the same medium a carboranylmercury salt gives two two-electron waves, the first corresponding to reduction to Hg^0 and carborane, and the second to reduction of the latter. As was to be expected, the introduction of substituents into the ferrocene ring system affects the half-wave potentials of both waves on polarograms of ferrocenylmercuric chloride, but the shifts are very small[35], which is consistent with the low-transmission of the induction effect of one ferrocene ring into the other.

It has recently been shown[36] that transfer of the first electron may occur either reversibly or irreversibly depending on the conditions. Thus allyl- and phenylmercuric halides give reversible waves in aqueous ethanol (1 : 1) and in ethanolic benzene (1 : 1), whereas in aqueous dimethylformamide and acetonitrile the first waves are irreversible with their half-wave potentials independent of the nature of the halide.

As already noted, the second reduction waves on polarograms of organomercury salts correspond to reduction of the "organic calomel" by reaction (5). Their half-wave potentials often depend on pH in acid media, but not in alkaline media[2]. In view of the possible reversible disproportionation (4) it might be expected that the symmetrical organomercury compounds R_2Hg formed by this reaction would be reduced at the same potentials as are the $RHg\cdot$ radicals. In fact, however, the waves of symmetrical organomercury compounds are usually situated at more negative potentials than are those of R_2Hg_2. The presence of separate R_2Hg_2 and $R_2Hg\cdot$ waves is due to the comparatively low rate of establishment of equilibrium (4).

The difference between the half-wave potentials for the reduction of HgR_2 and $RHg\cdot$ is smaller the lower the absolute value for the former[35]. If an organomercury salt is reduced very readily, the difference between the half-wave potentials of first and second waves becomes small, so that sometimes (e.g. with carboranylmercury salts) the two waves coalesce into a single two-electron wave[35].

A linear relation exists between the half-wave potential of the second reduction wave of RHgX and the electron affinity of the radical $R\cdot$. This enables the electron affinity of the radical to be estimated from polarographic data[35].

Symmetrical organomercury compounds. These are reduced irreversibly in a single stage involving two electrons[37]:

$$R_2Hg + 2e + 2H^+ \rightarrow 2RH + Hg.$$

The half-wave potential is usually unaffected by solution pH. Such an effect, i.e. preceding protonation, occurs only when R contains basic groups (e.g. carbonyl).

In some cases a symmetrical compound adsorbed on the mercury electrode reacts quite rapidly with the mercury to form free radicals $RHg\cdot$ or an organic calomel[9], which are reduced at less negative potentials. Two waves are then observed on the polarograms, the second corresponding to reduction of the symmetrical compound that has not reacted with mercury[9].

The ease of reduction of R_2Hg depends on the polarity of the R–Hg bond: the more polar this bond, the more readily does reduction take place[37]. Organomercury compounds containing an α-oxo-group are reduced most easily. Thus for the reduction wave of $(C_6H_5CHCOOC_2H_5)_2.Hg$ in 0.1 M sodium tetrafluoroborate in 50% aqueous methanol $E_{\frac{1}{2}} = -0.36$ V (s.c.e.), whereas the corresponding potential for dibenzylmercury under the same conditions is -1.64 V.[37] In 0.1 M tetraethylammonium perchlorate in dimethylformamide diphenylmercury gives a wave with $E_{\frac{1}{2}} = -2.21$ V (relative to 0.1 M $(C_2H_5)_4NI/Hg_2I_2$ in dimethylformamide).

The most positive value $E_{\frac{1}{2}} = -0.18$ V (s.c.e.) has been obtained for the reduction wave of mercury dicyanide in water, the wave being reversible[38], in contrast to other symmetrical organomercury compounds. Diferrocenylmercury, in contrast, is reduced at extremely negative potentials (in 0.1 M tetrabutylammonium perchlorate in dimethylformamide $E_{\frac{1}{2}} \simeq -2.68$ V aq.s.c.e.).[35]

Diphenylmercury. In tetrabutylammonium perchlorate dissolved in dimethoxyethane this compound gives a wave with $E_{\frac{1}{2}} = -3.32$ V (relative to an $Ag/AgClO_4$ (10^{-3} M) electrode). The half-wave potentials for the reduction of perchlorodiphenylmercury and perfluorodiphenylmercury under the same conditions are respectively -2.63 and -1.81 V.[14]

Perfluorodiphenylmercury. In a 1 M solution of sodium perchlorate in 30% aqueous methanol the polarograms contain one two-electron diffusion wave with $E_{\frac{1}{2}} = -1.06$ V (s.c.e.) independent of pH. The galvanostatic reduction of multilayers of perfluorodiphenylmercury adsorbed on the mercury electrode exhibits only one arrest at low current densities, but two at high current densities, the first corresponding to reduction of the first layer, and the second to reduction of the remaining layers[25]. Perfluorodiphenylmercury has been used as model compound to study the effect of the structure of the electrical double layer on the reduction of an adsorbed depolariser[39], as well as the effect of partial desorption of the depolariser on the capacitive section of the charging curve in the galvanostatic reduction of a substance adsorbed on the surface of a suspended mercury drop[40].

Bis-5-acetylthien-2-ylmercury. In a 1.0 M solution of sodium perchlorate in 30% aqueous dimethylformamide this gives two waves, the first of which ($E_{\frac{1}{2}} = -1.29$ V) corresponds to rupture of carbon–mercury bonds, and the second to reduction of the acetylthiophen formed[27].

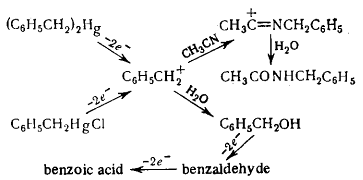
Bis-2,5-diphenyl-1,3-oxazol-4-ylmercury. With linear variation of the potential at a stationary platinum disc electrode in dimethylformamide the volt–ampère curves contain three reduction peaks[41]. With a rate of change of the potential $V = 20$ mV s^{-1} the potential of the first peak $E_p = -1.96$ V (s.c.e.) becomes more cathodic with increase in V, which indicates an irreversible chemical reaction following reversible electron transfer. The ratio of the peak current to $V^{\frac{1}{2}}$ increases with V, which is characteristic of a process with weak adsorption of the depolariser[42]. The first peak corresponds to rupture of carbon–mercury bonds; the other two peaks represent reduction of the mercury-free oxazoline derivative formed.

Bis-2-piperidinoethylmercury. In 50% aqueous ethanol this is reduced to piperidine ($E_{\frac{1}{2}} = -1.5$ V), but it gives no reduction waves in dimethylformamide[26].

The slopes of the waves (i.e. the experimental apparent transfer coefficients $\alpha_{\exp}$) vary greatly for different organomercury compounds. This is one reason for the absence of a strict correlation between the half-wave potentials and the Taft (or Hammett) σ-values of substituents. However, derivatives of dibenzylmercury with various substituents in the ring (when $\alpha_{\exp}$ remains approximately constant) satisfy the correlation $E_{\frac{1}{2}} = 2\sigma\rho$ fairly well, where σ is the Hammett constant of the substituents, the factor 2 reflects the presence of two groups in both benzene rings, and $\rho = +0.49$ V.[37] A good correlation is observed also between the product $\alpha_{\exp}E_{\frac{1}{2}}$ and the acid dissociation exponent pK_a of the hydrocarbon RH formed by the radical R.[19,37] It formed the basis of a proposed acidity scale for CH acids of saturated, aromatic, and unsaturated hydrocarbons, polyfluorinated and carbonyl-containing compounds, barenes, and certain other compounds[43]. However, it has been found[44] that the pK_a of CH acids correlate better with $E_{\frac{1}{2}}$ than with the product $\alpha_{\exp}E_{\frac{1}{2}}$; values of p$K_a$ have been estimated[44] for ferrocene and for the cyclopentadienyltricarbonyls of manganese and rhenium.

The polarographic method has been used to study the kinetics and the equilibria in the reaction of diphenylmercury with mercury dicyanide, bistrichloromethylmercury, and mercury bisphenylacetylide[45], as well as of diphenyl- and di-*p*-methoxybenzyl-mercury with certain symmetrical carbonyl-containing organomercury compounds in dimethylformamide solution[46].

Application of a linearly varying potential to a rotating platinum anode in acetonitrile with 0.1 M sodium perchlorate as supporting electrolyte gives with organomercury compounds clear oxidation waves having half-peak potentials (with $V = 20$ V s^{-1}) of 1.28, 1.53, 1.58, 1.95, and 1.84 V (relative to silver in 0.01 *N* silver perchlorate) for n-propylmercuric chloride, benzylmercuric chloride, dibenzylmercury, phenylmercuric tetrafluoroborate, and diphenylmercury respectively. The waves are completely irreversible. The results of preparative electrolysis in acetonitrile alone and with water (10%) suggested the following schemes



i.e. the first stage always involves rupture of a carbon–mercury bond and formation of a carbonium cation. In the presence of water the process is influenced by the anions of the supporting electrolyte[47].

II. ORGANOMAGNESIUM COMPOUNDS

Dialkylmagnesium derivatives. When dissolved in dimethoxyethane these compounds R_2Mg give anodic oxidation waves having $n = 2$ (the products are R_2Hg and Mg^{2+}), but are not reduced: reduction waves (with $n = 1$) are observed only when R forms a comparatively stable carbanion[48]. Half-wave potentials for reduction (relative to the 10^{-3} M $AgClO_4/Ag$ electrode) are −2.74, −2.65, and −2.50 V when R is respectively benzyl, allyl, and cyclopentadienyl. The mechanism of the process can be written[48]

$$R_2Mg + e \rightarrow R^{-}: + RMg^{\cdot} \rightarrow Mg^0 + R^{\cdot}\left[\begin{array}{l} \xrightarrow{\text{detachment of } H^{\cdot}} \\ \xrightarrow{\text{dimerisation}} \\ \xrightarrow{\text{disproportionation}} \end{array}\right.$$

Grignard reagents. Both the "natural" and the "synthetic" reagents, RMgX and $R_2Mg + MgX_2$ mixtures, give two reduction waves except with $R = CH_3$, when only one wave is observed. Coulometric electrolysis on the current plateau of both first and second waves gives $n = 1$, with the half-wave potential of the first wave close to that of MgX_2 (−2.47 V), and that of the latter lying between −2.70 and −2.80 V. The mechanism of the process was explained[48] in terms of rapid establishment of the Schlenk equilibrium

$$2RMgX \rightleftarrows MgX_2 + MgR_2 \qquad (7)$$

and reduction of MgX_2 in the first stage.

A pulsed galvanostatic study (with reversal of current) of a Grignard reagent at a magnesium electrode in diethyl ether indicates the occurrence of both cathodic and anodic processes (formation and dissolution of Mg^0). The introduction of oxygen, acetone, or bromoethane into the solution changes the form of the curves[49]. In ether and oxolan the reduction of Grignard reagents at a bright platinum cathode gives metallic magnesium; on anodic oxidation alkanes and alkenes are formed[50].

Polarisation curves have been determined for the oxidation of alkylmagnesium chlorides at rotating platinised and smooth platinum and also gold electrodes in oxolan solutions[51]. Fairly high concentrations (0.2–0.6 M) of the depolarisers were taken to ensure adequate electrical conductivity of the solution without addition of an inert electrolyte. Oxidation takes place most readily on platinised platinum, with rather greater difficulty on a gold electrode, and with the greatest difficulty on smooth platinum. The sequence of diminishing ease of oxidation of Grignard derivatives containing different groups is t-butyl > ethyl > isopropyl, vinyl > n-butyl > methyl > phenyl. The course of the reduction by these Grignard reagents in oxolan of naphthacene (at concentrations of 5×10^{-6} M and 5×10^{-4} M) to the radical-anion was followed by the determination of current–potential curves at rotating platinum and gold electrodes. The sequence of diminishing ease of oxidation of RMgCl coincides with their decreasing ability to reduce hydrocarbons[51].

Current–potential curves have been obtained at a rotating platinised platinum electrode in argon and in a mixture of argon with hydrogen at different pressures of the latter (i.e. at a hydrogen electrode) in oxolan with lithium and tetrabutylammonium perchlorates, as well as in the absence of a supporting electrolyte (for high depolariser concentrations), for several Grignard reagents and disubstituted organomagnesium compounds[52]. The oxidation of such reagents can be described by the general equation

$$2RMgCl \rightarrow R{-}R + 2e + 2MgCl^+,$$

or

$$2RMgCl \rightarrow R_{H(-1)} + RH + 2e + 2MgCl^+,$$

i.e. with dimerisation and dimutation respectively of the radicals formed ($R_{H(-1)}$ denotes an alkene formed from R).

The current observed on cathodic polarisation in argon probably corresponds to the process

$$\mathrm{RH} + \mathrm{MgCl}^{+} + e \rightarrow \mathrm{RMgCl} + \frac{1}{2}\mathrm{H}_2,$$

where RH has been formed owing to decomposition of RMgCl by traces of moisture[52]. Introduction of hydrogen into the solution leads to a clear anodic wave, whose height increases with the partial pressure of hydrogen. For methylmagnesium chloride this wave probably corresponds to the process

$$\mathrm{CH_3MgCl} + \frac{1}{2}\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + e + \mathrm{MgCl}^{+},$$

i.e. to the oxidation of hydrogen catalysed by the Grignard reagent (the concentration of the latter far exceeds that of hydrogen), so that the height of the wave corresponds to a diffusion current of dissolved hydrogen. This anodic wave, together with the cathodic wave for the reduction of methane catalysed by MgCl^{+}, represents a redox system, in which the zero-current potential at the hydrogen electrode corresponds to the equilibrium potential of the system. Under otherwise similar conditions the latter depends on the basicity of the Grignard reagent (or, in view of the Schlenk equilibrium (7), to $\mathrm{R_2Mg}$), which in turn enables the basicity of a series of Grignard reagents to be determined quantitatively from current–potential curves at a hydrogen electrode[52]. An alkylmagnesium chloride was found to be rather more basic than the bromide. In oxolan some dissociation of RMgX to RMg^{+} and X^{-} takes place[52].

At a lead anode in 0.25 M tetrabutylammonium perchlorate in oxolan diethylmagnesium and ethylmagnesium bromide give very clear oxidation waves having half-wave potentials of −1.72 and −1.73 V (relative to Ag/0.01 M $\mathrm{AgClO_4}$ in oxolan). The wave heights are around one-tenth of the diffusion currents and are determined by reactions with the lead electrode. Tetraethyl-lead is the final product in both cases[53]. Chemical interaction of these depolarisers with lead explains their far greater ease of oxidation on a lead than on a platinum anode[53].

III. ALUMINIUM DERIVATIVES

Sodium tetraethylaluminate. At a lead microelectrode in 0.25 M tetrabutylammonium perchlorate in oxolan this compound $\mathrm{NaAl(C_2H_5)_4}$ gives a sharp oxidation wave with $E_{\frac{1}{2}} = -1.25$ V (relative to Ag/0.01 M $\mathrm{AgClO_4}$ in oxolan). The height of the wave is limited by preceding chemical reaction of the depolariser and the intermediate product with the lead electrode. The final anodic oxidation products are triethylaluminium and tetraethyl-lead[53].

Triethylaluminium. Under the same conditions this compound is not oxidised at a lead electrode up to potentials at which lead dissolves (−0.6 V).[53]

Aluminium isopropoxide. At high concentrations (down to 0.1 M) in absolute propan-2-ol, with lithium chloride as supporting electrolyte, this derivative gives at a dropping mercury electrode a small kinetic cathodic wave representing discharge of hydrogen atoms with $E_{\frac{1}{2}} = -1.45$ V (relative to silver in the same solution).[54]

IV. BORON COMPOUNDS

Tetraphenylborate ion. Two oxidation peaks are obtained at a graphite anode in aqueous solutions[55,56]. The first peak corresponds to the process

$$\mathrm{B(C_6H_5)_4^{-}} - 2e \rightarrow \mathrm{(C_6H_5)_2} + \mathrm{B(C_6H_5)_2^{+}},$$

$$\mathrm{B(C_6H_5)_2^{+}} + \mathrm{H_2O} \rightarrow \mathrm{B(C_6H_5)_2OH} + \mathrm{H^{+}}.$$

This wave is independent of pH, and its half-peak potential $E_{p/2} = 0.216$ V (relative to a saturated NaCl–calomel electrode). The second peak represents the process

$$\mathrm{B(C_6H_5)_2OH} - 2e + 2\mathrm{H_2O} \rightarrow \mathrm{B(OH)_3} + \mathrm{(C_6H_5)_2} + \mathrm{H^{+}},$$

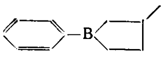
its half-peak potential depending on the pH:[56]

$$E_{p/2} = 0.92 - 0.057\mathrm{pH}.$$

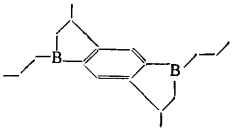
At a graphite anode two waves are obtained also in anhydrous acetonitrile and dimethylformamide with lithium perchlorate as supporting electrolyte[56]. At a platinum anode only one wave can be observed[57], but after appropriate anodic treatment of the electrode surface both oxidation waves of the tetraphenylborate ion can be observed also on platinum[58].

1,2′-Bis(diphenyl)borate ion. This gives a single two-electron wave on current-potential oxidation[59].

Dialkylborons and diarylborons. A compound such as $\mathrm{R_2B}$ behaves as a pseudometallic ion[60]. Its complexes with acetylacetone (AcAc) in tetrabutylammonium perchlorate in monoglyme give irreversible one-electron diffusion waves with half-wave potentials (V, relative to 1mM $\mathrm{Ag^{+}/Ag}$ electrode) of −2.16, −2.40, and −2.66 for the diphenylethynyl, diphenyl, and diethyl derivatives[60]. Electrolysis of $\mathrm{(C_6H_5)_2BAcAc}$ at −2.48 V gave a product which, on anodic oxidation at −0.3 V, regenerates the initial compound $\mathrm{(C_6H_5)_2BAcAc}$. Complexes of $\mathrm{BR_2}$ with 1,3-diphenylpropane-1,3-dione all give two one-electron waves, with half-wave potentials of −1.60 and −2.66 V for diethylboron, and −1.90 and −2.80 V for diphenylboron[60].



(I)



(II)

Phenylborolan (I) and diborindacene (II). With 0.1 M tetrabutylammonium iodide in anhydrous dimethylformamide methyl derivatives of (I) and derivatives of (II) give reversible one-electron waves corresponding to formation of the radical-anion, with half-wave potentials respectively of −1.96 and −1.46 V (relative to the mercury at the base of the cell); the corresponding potentials for the naphthalene and anthracene waves under the same conditions are −1.94 and −1.48 V. Thus the introduction of boron facilitates appreciably transfer of an electron to the aromatic π-electron system[61]. Polarograms of diborindacene contain also a second reduction wave, representing an irreversible electrode process.

Dibutyl benzeneboronate and tetrabutyl benzene-*p*-diboronate. The products $\mathrm{C_6H_5B(OC_4H_9)_2}$ and $\mathrm{(C_4H_9O)_2BC_6H_4B(OC_4H_9)_2}$ of the atmospheric oxidation or the hydrolysis of the preceding compounds are also reduced under the above polarographic conditions, with half-wave potentials of −2.02 and −1.93 V respectively[61].

Barenes (carboranes). These are polyhedral aromatic systems containing boron $B_{10}H_{10}C_2RR'$. In 0.1 *N* tetraethylammonium perchlorate in dimethylformamide they give diffusion reduction waves, with half-wave potentials of −2.51 and −2.8 V (s.c.e.) for barene (*o*-barene) and neobarene (*m*-barene) respectively[62], whereas *p*-barene gives no wave[30]. Substitution of phenyl at position 1 (at a carbon atom) facilitates reduction appreciably (half-wave potentials of −1.95 and −2.45 V for 1-phenyl-*o*-barene and 1-phenyl-*m*-barene), but 3-phenyl-*o*-barene (−2.59 V) is reduced with greater difficulty than is *o*-barene itself[62]. Study of many derivatives has established that the effect of substituents on half-wave potentials is more marked with *o*- than with *m*-barenes[62]. It is noteworthy that the reduction of *o*-barene is facilitated by introduction of a 1-methyl group[62,63]. The reduction of barenes involves transfer of a single electron, probably with formation of a radical-anion[63].

C-Halogenated barenes. Polarograms obtained in dimethylformamide usually contain two waves, the first of which, representing electrochemical cleavage of the carbon–halogen bond, is double the height of the second wave. Derivatives of *o*-barene are most readily reduced, and those of *p*-barene with the greatest difficulty[63]. In contrast to the situation with halogen derivatives of benzene and benzyl, 1-chloromethyl- and 1-bromomethyl-*o*-barenes (with half-wave potentials of −2.03 and −1.21 V s.c.e.) are reduced with greater difficulty than are 1-chloro- and 1-bromo-barene respectively (−1.19 and −0.56 V).[63] 1,12-Dihalogeno-*p*-barenes give two two-electron waves representing the detachment of halogen[63]. The half-wave potentials become more negative on passing from *C*-iodo- to *C*-bromo- and *C*-chloro-derivatives of barenes. For example, values for the 1-halogenated *p*-barenes in dimethylformamide with tetradecylammonium perchlorate as supporting electrolyte are respectively −0.53, −0.99, and −2.14 V (s.c.e.).[64] It is interesting that these compounds are not reduced at a platinum electrode.

B-Halogenated barenes. These derivatives are reduced with very great difficulty, and their half-wave potentials are almost independent of the nature of the halogen. Thus for 10-halogeno-*o*-barenes in 0.1 M tetrabutylammonium bromide in dimethylformamide they are close to −2.18 V (s.c.e.).[64]

Di-*o*(and *m*)-barenylmercury. These compounds and their derivatives give reduction waves in dimethylformamide, whose half-wave potentials have been used[65] to estimate the acidity of carbon–hydrogen bonds in corresponding derivatives of *o*- and *m*-barenes. For the same purpose several dibarenylmercury derivatives (*ortho*, *meta*, and *para*) have been investigated polarographically in various solvents[66].

Phosphacarboranes. These are reduced somewhat more readily than are carboranes, the ease of reduction diminishing as with the latter in the sequence of isomers *ortho*, *meta*, and *para*.[67] For *o*-phosphacarborane in dimethylformamide with 0.1 M tetrabutylammonium perchlorate $E_{\frac{1}{2}} = -2.30$ V (s.c.e.).

Arsacarboranes. The half-wave potentials become more negative in the sequence *meta*, *para*, *ortho*. On the polarogram of the *ortho*-isomer the main wave is preceded by a prewave hump. *m*- and *p*-Arsacarboranes are reduced somewhat more readily than are the corresponding isomeric phosphacarboranes[67].

V. THALLIUM COMPOUNDS

Dialkylthallium bromide. In 30% aqueous propan-2-ol buffered to pH 7 the polarograms for the n-propyl and n-butyl derivatives R_2TlBr contain three waves of approximately the same height, the first and the third of which are diffusion waves. The first wave is preceded by an adsorption prewave[68], and corresponds to the process

$$2R_2Tl^+ + 2e \rightarrow (R_2Tl)_2$$

with half-wave potentials respectively of −0.922 and −0.895 V. Diethylthallium bromide, in contrast to its homologues, does not give prewaves on the polarograms, and its first wave ($E_{\frac{1}{2}} = -1.000$ V) corresponds to the transfer of two electrons, probably with the formation of ethylthallium(I).[68] In aqueous Britton–Robinson buffers of pH < 7 dialkylthallium bromides give a sharp one-step wave, whose half-wave potential is independent of pH and becomes more positive with growth of the alkyl chain, from −1.07 V for methyl to −0.92 V for n-pentyl. At pH > 7 a second wave is observed, and is attributed to reduction of hydrolysis products[69]. In dimethylformamide dialkylthallium bromides give four cathodic waves, the third and fourth of which become more positive on addition to the solution of phenol (as a proton donor). In excess of the donor only two waves are observed, the ratio of whose heights is 1 : 2, which corresponds to reduction to $R_2Tl\cdot$ and then to Tl^0 respectively[69]. In the absence of proton donors the primary product of one-electron reduction $R_2Tl\cdot$ either disproportionates to Tl^0 and R_3Tl or is reduced further to Tl^0. In the presence of such donors dialkylthallium cations are rapidly regenerated:

$$R_3Tl + H^+ \rightarrow R_2Tl^+ + RH\ .$$

Therefore a one-step reduction wave of R_2Tl is observed in acid aqueous solutions[69].

Trialkylthallium derivatives. In dimethylformamide such compounds are probably reduced[69] in two stages:

$$2R_3Tl + 2e \rightarrow [R_6Tl_2]^{2-},$$

$$[R_6Tl_2]^{2-} + 4e \rightarrow 6R^- + 2Tl^0.$$

Triphenylthallium(III). In dimethylformamide this gives two waves, with half-wave potentials −1.76 and −2.55 V.[69]

Diphenylthallium chloride. With 0.05 M tetraethylammonium perchlorate in dimethylformamide this gives two waves, having half-wave potentials −0.79 and −2.58 V (aq. s.c.e.) respectively[70]. After such a solution has stood over mercury for a long time (several days), however, the [first] wave falls, and a new wave ($E_{\frac{1}{2}} = -0.46$ V), corresponding to the discharge of Tl^+ ions, appears in front of it. Thus diphenylmercury may be formed at a mercury electrode not only by the cathodic reduction of diphenylthallium (see below) but also as a result of its reaction with mercury[70].

Diphenylthallium(III) cation. Polarograms obtained in aqueous phosphate buffers contain three reduction waves, the heights of the first two being proportional to the depolariser concentration and restricted by diffusion, while the third wave tends to a limit with increase in concentration[71]. The half-wave potentials of the first and third waves become more negative with increase in the diphenylthallium concentration, whereas that of the second wave becomes more positive; those of the second and third waves vary with pH, but that of the first wave does not. Electrocapillary curves obtained during the drop period indicate strong adsorption of the starting material and still greater adsorption of intermediate reduction products. On preparative electrolysis at the limiting-current potentials of all three waves 1 mole of Tl^0 is formed as an amalgam and various quantities of diphenylmercury per mole of the initial substance, accompanied on the second and third waves by benzene[71]. The primary process is transfer of a single electron:

$$(C_6H_5)_2Tl^+ + e \rightarrow Tl^{\cdot}(C_6H_5)_2.$$

The resulting radical reacts in several ways: it interacts with mercury

$$(C_6H_5)_2Tl^{\cdot} + Hg \rightarrow (C_6H_5)_2Hg + Tl^0,$$

or disproportionates in the adsorbed state on mercury, giving diphenylmercury, Tl^0 and triphenylthallium, which is rapidly hydrolysed to benzene and diphenylthallium (reduction of the latter is the reason for the > 1 electrons determined coulometrically for the first wave). The radical $(C_6H_5)_2Tl\cdot$ may also be hydrolysed to benzene and inorganic thallium derivatives, which are reduced at the dropping mercury electrode. The second wave corresponds to the transfer of one electron to the diphenylthallium radical with formation of benzene and phenylthallium (I), which reacts rapidly with mercury

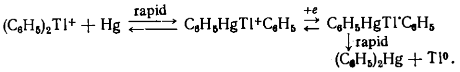
$$2Tl(C_6H_5) + Hg \rightarrow (C_6H_5)_2Hg + Tl^0.$$

The third wave corresponds to the process

$$C_6H_5Tl + e \xrightarrow{H^+} C_6H_6 + Tl^0.$$

Half-wave potentials in 1 mM solution at pH 7 are respectively −0.62, −0.94, and −1.42 V (s.c.e.).[71]

Diphenylthallium derivatives. A different interpretation has been given[70] of the mechanism of reduction. Derivatives with *para*-substituents (methoxy, methyl, chloro, methoxycarbonyl) and the *m*-tolyl derivative exhibit three reduction waves in aqueous 1 M potassium acetate, the first two of which are diffusion waves, whereas the limiting current of the third wave is determined by adsorption phenomena. The first wave is regarded[70] as preceded by very rapid reaction between the thallium derivatives and mercury, to give a product that acquires an electron reversibly:



$$\begin{array}{l} (C_6H_5)_2Tl^+ + Hg \underset{}{\overset{\text{rapid}}{\rightleftarrows}} C_6H_5HgTl^+C_6H_5 \overset{+e}{\rightleftarrows} C_6H_5HgTl^{\cdot}C_6H_5 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{rapid} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (C_6H_5)_2Hg + Tl^0. \end{array}$$

The second wave corresponds to further reduction of $C_6H_5HgTl(C_6H_5)\cdot$ involving two electrons. However, the height of the second wave does not reach the diffusion current corresponding to the transfer of two electrons (probably because of retardation of the electrode process by substances, mainly diphenylmercury, adsorbed on the electrode). Desorption of diphenylmercury takes place at the potential of the third wave, so that the latter corresponds to reduction of depolariser that has not been reduced under the conditions of the second wave; a jump in the capacitive current due to the desorption of diphenylmercury is superimposed on the Faraday current of the third wave. This scheme of reduction is supported by the results of a chronopotentiometric study of diphenylthallium derivatives[70].

At a platinum microcathode in anhydrous dimethylformamide the diphenylthallium cation gives two irreversible diffusion waves, with half-wave potentials of −0.85 and −1.70 V (s.c.e.). The first corresponds to the transfer of one electron and the formation of diphenylthallium radicals, which disproportionate to give metallic thallium and triphenylthallium. Reduction of the latter gives the second wave, whose height is double that of the first wave[73]. The reduction of triphenylthallium yields Tl^0 and benzene. The primary products of electrolysis at −30°C are Tl^0 and $(C_6H_5)_4Tl^-$.[73]

Phenylthallium(III). Polarograms obtained in aqueous media contain an adsorption prewave and three one-electron diffusion waves. The half-wave potentials of the first and second waves are independent of depolariser concentration and of pH (−0.01 and −0.50 V (s.c.e.) respectively). That of the third wave becomes more negative with increases in both factors. Electrolysis at the limiting current of the first wave gives diphenylmercury and Tl^+; at that of the second wave Tl^0 accompanies diphenylmercury; and the third wave corresponds to reduction of phenylthallium(I) formed in the preceding stage[72]. In dimethylformamide diphenylthallium bromide and phenylthallium dichloride give two waves, the first representing reduction to Tl^0, and the second ($E\frac{1}{2} = -2.55$ V) reduction of diphenylmercury[69].

VI. DERIVATIVES OF GROUP IV ELEMENTS—THE SILICON SUBGROUP

Organochlorosilanes. Reduction waves were obtained[74] in anhydrous acetone, though their reproducibility was poor. Waves that can be used for the quantitative determination of organochlorosilanes were obtained in pyridine and its aqueous mixtures[74]. The wave then corresponds to discharge of the pyridinium ion formed by solvolysis of the organochlorosilane.

Ethyltrichlorogermane. In a benzene–methanol (3 : 2) mixture with 0.1 *N* lithium chloride as supporting electrolyte a sharp three-electron diffusion wave is obtained, corresponding to detachment of all the chlorine atoms and formation of the radical $C_2H_5Ge\cdots$, which gives a polymeric product. The wave observed in acidic aqueous solutions (to pH 4.0) is distorted by strong adsorption of the initial depolariser and the reaction products; with increase in depolariser concentration the height of the wave reaches a limit (at $c > 0.5$ mM), while its half-wave potential becomes more negative. Electrocapillary and current–time curves showed that rearrangement of the adsorbed layer occurs in the lower part of the wave at −1.06 V (s.c.e.): depolariser on the electrode surface is replaced by the reaction product. In methanolic benzene neither the depolariser nor the reaction product is adsorbed on a mercury electrode[75].

Mono- and bis-trimethyl-silyl, -germyl, and -stannyl derivatives of biphenyl. Derivatives with the substituents in positions 4 or 4 and 4′ give in anhydrous dimethylformamide reversible waves corresponding to the formation of radical-anions; the half-wave potentials lie in the range −1.94 to −2.07 V relative to the potential of the mercury at the bottom of the vessel (the supporting electrolyte is not indicated). Silicon derivatives are rather more electropositive than the germanium derivatives, while the tin derivatives are the most electronegative[76].

Bistrimethyl-silyl and -germyl derivatives of polyphenylenes. In dimethylformamide these derivatives $(CH_3)_3M[C_6H_4]_mM(CH_3)_3$ (where m = 1–4 and M = Si, Ge) give reversible one-electron waves, except in the case of *p*-bistrimethylgermylbenzene, which is polarographically inactive. Polyphenyl derivatives give a second one-electron wave, corresponding to formation of a dianion. The instability of the latter, leading to detachment of trimethylsilyl or trimethylgermyl groups, is responsible for the incomplete reversibility of the second wave. The half-wave potential of the first wave becomes more positive with increase in m, while the reversibility of the second wave improves[77].

In order to determine how the silyl bridge influences conjugation between two diphenylyl groups, ordinary and a.c. polarograms (with recording of the signal from the principal and second harmonics) have been obtained[78] on several compounds. The first waves correspond to reversible transfer of one electron (redox potentials E^0 given in parentheses for the first reduction waves in dimethylformamide with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and silver in a saturated dimethylformamide solution of tetrabutylammonium iodide as reference electrode). The compounds investigated were 4-trimethylsilylbiphenyl (−1.897), 4,4′-bistrimethylsilylbiphenyl (−1.805), dibiphenyl-4-yldimethylsilane (−1.853), 4,4′-bisbiphenyl-4″-yldimethylsilylbiphenyl (−1.750), and for comparison the hydrocarbons biphenyl (−1.999), dibiphenyl-4-ylmethane (−2.019), and 4,4′-di-*p*-phenylbenzylbiphenyl (−2.024). Thus introduction of a silyl group shifts the redox potential to less negative values than for the corresponding hydrocarbon. However, comparison with the ultraviolet spectra indicated[78] that a silyl bridge largely prevents conjugation between two biphenylyl groups.

1-Naphthylpolysilanes. A study has been made[79] of the polarographic behaviour of the compounds (Ar = 1-naphthyl and Me = CH_3)—$ArSiMe_3$, $ArSiMe_2Ar$, $ArSi_2Me_5$, $Ar[SiMe_2]_2Ar$, $ArSi_3Me_7$, $Ar[SiMe_2]_3Ar$, and $ArCH_2SiMe_3$—as well as of naphthalene and 1-methylnaphthalene for comparison. With 0.05 M tetrabutylammonium iodide in dimethylformamide mononaphthyl derivatives give one reversible one-electron diffusion wave, and dinaphthyl derivatives two such waves. Half-wave potentials for the above compounds (measured by a three-electrode scheme relative to Ag/0.1 M $AgNO_3$ in dimethylformamide) are respectively (values for the second wave given in parentheses) −2.845, −2.781 (−3.038), −2.842, −2.816 (−2.983), −2.838, −2.822 (−2.924), −3.006, −2.946, and −2.964 V. Introduction of a trimethylsilyl group facilitates electron transfer to the naphthalene ring system; facilitation is still greater on introduction of a second naphthalene ring system at the end of the silyl chain. With increase in length of this chain, however, the effect of the second ring system diminishes (the half-wave potential becomes more negative), while transfer of a second electron to the second ring system is facilitated, which indicates diminished transmission of the effect through the silyl bridges[79].

1,4-Bistrimethylsilyl(and germyl) naphthalenes. These give a single reversible one-electron wave. The silicon derivatives are reduced rather more easily than are the germanium derivatives[77]. Introduction of a trimethylsilyl group into the naphthalene molecule shifts the reversible one-electron reduction wave (with 0.1 M tetrabutylammonium iodide in dimethylformamide) to less cathodic potentials (by ~ 50 and by ~ 10 mV in positions 1 and 2 respectively); reduction is still more facilitated by the introduction of two groups, reaching 150 mV with 1,4-bistrimethylsilyl derivatives. However, introduction into the naphthalene molecule of a t-butyl group (or of two such groups) impedes reduction: the maximum effect is ~ 110 mV with the 2,7-di-t-butyl derivative[80].

Iodotrialkylsilylalkanes. Cleavage of the carbon–iodine bond is somewhat facilitated by introduction of a trialkylsilyl group into an iodoalkane, although this effect may be due not only to the electronegative action of the group but also to enhanced adsorbability of the organic molecule[81]. An important consequence of such introduction is to stabilise the free radical[82] formed as intermediate in the reduction of iodo-derivatives. Such stabilisation results in division of the two-electron wave into two one-electron steps, the half-wave potentials of both of which correlate with the electronegativity of the trialkylsilyl substituent[82].

Other evidence indicates the electron-accepting properties of the trialkylsilyl group. Thus introduction of the group into the *para*-position of nitrobenzene facilitates reversible transfer of the first electron to the nitro-group (in anhydrous dimethylformamide) by ~ 100 mV.[83] Reduction of mono- and di-silanaphthenes in dimethylformamide is facilitated by 200–400 mV in comparison with naphthalene, whereas acenaphthene itself is reduced with rather greater difficulty than is naphthalene[84]. The silicon atom in 5,10-dihydro-5,5-dimethyldibenzo[*b*,*e*]silinone competes slightly[85] even with the carbonyl group, facilitating electrochemical reduction of the latter (the half-wave potential of the reversible one-electron wave in dimethylformamide is −1.64 V relative to mercury in 0.1 M tetrabutylammonium perchlorate solution).

Phenyltrimethylsilane. On reduction in anhydrous methylamine solution at a platinum cathode in the presence of lithium chloride in a cell with a diaphragm, products resulting from detachment of the trimethylsilyl group and hydrogenation of benzene are obtained. In the absence of a diaphragm the main reduction product is *p*-dihydrophenyltrimethylsilane resulting from the action of lithium methylamide formed at the anode[86].

Triphenylsilyl and triphenylgermyl chlorides. In anhydrous dimethoxyethane these compounds give a one-electron wave with half-wave potentials of −3.1 and −2.8 V relative to an Ag/$AgClO_4$ (1 mM) electrode. The products were regarded as formed by the replacement of chlorine by hydrogen atoms, but the source of the atomic hydrogen was not indicated[87].

Halogenated triphenylgermanes. In an extremely detailed study[88] 1,2-dimethoxyethane was used as solvent, with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and silver in a saturated solution of silver nitrate in the same solvent as reference electrode

Triphenylfluorogermane. The slope suggests that the single polarographic reduction wave is reversible, with $E_{\frac{1}{2}} = -3.1$ V and its height formally corresponding to a diffusion current with transfer of half an electron. When increasing quantities of an alcohol or water are introduced into the solution, a new wave appears and grows on the limiting-current plateau of the first wave (whose height and half-wave potential remain unaffected). The new half-wave potential is displaced to less negative values, so that in excess of these proton donors it reaches the height of the initial wave and merges with it to give a single irreversible one-electron diffusion wave.

Voltammetry with a linearly varying potential (in the absence of a proton donor) reveals only one cathodic peak, whose properties suggest that the process is irreversible. This implies that the process is in general quasi-reversible: the radical-anion formed by transfer of an electron to the initial molecule is assumed[88] to interact with another molecule of the initial compound to give an electrochemically inactive dimeric radical-anion, which explains the "half electron". The absence of an anodic peak of the radical in voltammetry with the application of triangular pulses indicates that the rate constant of formation of the dimer $[(C_6H_5)_3Ge(F)...GeF(C_6H_5)_3]^{\cdot}$ exceeds 10^5 M^{-1} s^{-1}. The dimer is obviously unstable, being slowly converted in solution into more stable compounds; this apparently explains the formation of a deposit of hexaphenyldigermane when the solution is allowed to stand after electrolysis.

Immediately after electrolysis bistriphenylgermyl oxide $[(C_6H_5)_3Ge]_2O$ was isolated, having been formed by reaction of the dimeric radical-anion with water or a peroxide, certain quantities of which are always present in the solvent. The anodic peak due to fluoride ions, present on current–voltage curves with reversal of potential, indicates quite rapid interactions of the dimeric radical in which fluoride ions are liberated. On the introduction of proton donors into the solution the dimeric radical-anion is protonated, after which it or a conversion product acquires a new electron, which corresponds to appearance of the new wave on the polarogram.

Triphenylchlorogermane. This gives an irreversible one-electron reduction diffusion wave having $E_{\frac{1}{2}} = -2.85$ V.[88] Addition of water or an alcohol does not affect the cathodic wave, but results in the appearance of an anodic one-electron diffusion wave. The cathodic process produces a triphenylgermyl radical and a chloride anion. The radicals dimerise to hexaphenyldigermane (the principal product of preparative electrolysis at high concentrations of the starting material), and react with peroxides to form triphenylgermyl hydroxide $(C_6H_5)_3GeOH$ and hexabiphenylyldigermyl oxide (the main product at low concentrations of the initial substance). A certain quantity of triphenylgermane is also formed on electrolysis, apparently as a consequence of abstraction of a hydrogen atom from the solvent (dimethoxyethane) by the germyl radical.

The anodic wave is due to interaction with mercury (which is absent at a platinum electrode):

$$(C_6H_5)_3GeCl \underset{Hg}{\xrightarrow{-e}} (C_6H_5)_3Ge^+ + \frac{1}{2}Hg_2Cl_2,$$

$$(C_6H_5)_3Ge^+ + ClO_4^- \rightarrow (C_6H_6)_3GeOClO_3.$$

Formation of a perchlorate with a covalent bond has been proved by ultraviolet spectroscopy of the product isolated after electrolysis on the current plateau of the anodic wave. Both this product and specially prepared triphenylgermyl perchlorate give a cathodic wave with $E_{\frac{1}{2}} \simeq -1.6$ V on the polarograms, whereas the corresponding potential for the cathodic wave of the solution immediately after anodic oxidation is -0.2 V. This is regarded[88] as indicating that the germanium cation formed gives initially with the perchlorate anion an ion-pair, which is then converted into the covalent compound.

Triphenylbromogermane. This behaves similarly to triphenylchlorogermane, with the sole exception that it gives an anodic wave even in the absence of water or an alcohol[88]. Half-wave potentials are -2.63 and -0.14 V for the one-electron cathodic diffusion wave and for the anodic wave respectively.

Triphenyliodogermane. The polarograms contain two cathodic waves with half-wave potentials of -1.9 and -2.45 V (the first is kinetically restricted, and the two waves give an aggregate diffusion current with $n = 1$) and a one-electron anodic wave with $E_{\frac{1}{2}} = -0.36$ V.[88] On the addition of water to the solution the first cathodic wave grows at the expense of the second; the anodic wave also diminishes, but a new anodic wave appears and grows ($E_{\frac{1}{2}} = -0.95$ V), and was shown to be due to an anodic process involving free iodide anions. The second wave also diminishes on electrolysis at the potential of the first cathodic wave; the sole product of electrolysis is hexaphenyldigermane oxide. The second wave corresponds to detachment of an iodide anion and formation of a triphenylgermyl radical; the first is attributed[88] to the processes

$$(C_6H_5)_3GeI + H_2O \rightleftarrows [(C_6H_5)_3GeIH]^+ + OH^-,$$

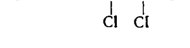
$$[(C_6H_5)_3GeIH^+] + e + OH^- \rightarrow (C_6H_5)_3Ge^{\cdot} + I^- + H_2O.$$

In excess of water the initial substance undergoes hydrolysis with formation of an iodide anion and triphenylgermyl hydroxide.

Alkylhalogenotin derivatives. These compounds $R_{4-x}Cl_xSn$ ($x = 1-3$) have been studied by many investigators[87,89-104], but the mechanism of their reduction has not yet been finally elucidated. Their electrode behaviour is complicated by very strong adsorption on the electrode both of the initial substances and of the reaction products[94,96,97,100-104], as well as by dissociation, which is responsible for the appearance of kinetic restrictions of the current[99,100,102]. Thus for dimethyldichlorotin[100] the height of the first wave (disregarding the adsorption prewave) falls with rise in pH along a curve resembling a dissociation curve (expressing the pH dependence of the concentration or proportion of the undissociated acid). At the same time a second wave appears and grows, so that the polarographic $pK'_a = 9.05$, which exceeds the potentiometrically determined exponents for the stepwise substitution of the chloride ion by the hydroxide ion ($pK_a = 4.5$ and 8.0[100]).

It has been shown for dichlorodiethyltin as example[100] that the total wave height corresponds to the transfer of only one electron, so that the process can be represented by the scheme[87,96,98]

$$R_2SnCl_2 + e \rightleftarrows R_2Sn^{\cdot}Cl + Cl^-, \quad (8)$$



$$2R_2Sn^{\cdot}Cl \rightarrow \underset{Cl}{\underset{|}{R_2Sn}}-\underset{Cl}{\underset{|}{SnR_2}}. \quad (9)$$

Addition of the electron occurs reversibly[96], with the resulting radicals dimerising on the electrode surface itself. The wave form (at low depolariser concentrations) is therefore[105] described by the equation[96]

$$E = \varepsilon_0 - 0.065\lg\frac{i^{1/2}}{i_{\text{lim}} - i}. \tag{10}$$

The system R_6Sn_2/R_3Sn^+ is reversible on a platinised platinum electrode in methanol alone and mixed with benzene ($R = C_6H_5$, CH_3, C_2H_5, C_4H_9).[106] With increase in the concentration of the depolariser (diethyldichlorotin) the wave separates into several steps[96-98], the first of which is similar in nature to a Brdička prewave (Brdička adsorption prewaves appear on polarograms with strong adsorption on the electrode of a reaction product or a complex with the initial depolariser, their height increasing with the depolariser concentration to a certain value corresponding to complete coverage of the electrode surface by a monolayer of the adsorbate, after which the prewave height remains unchanged with further increase in depolariser concentration). The appearance of two adsorption prewaves may be due[107] to layer-by-layer coverage of the surface.

A very important feature[98] of the polarographic behaviour of a dialkyldichlorotin is a gradual increase in the ratio of the total wave height to the depolariser concentration with increase in the latter, and also an increase in the number of electrons determined microcoulometrically, especially in acid media, which is attributed[98] to partial regeneration of the depolariser by the reaction

$$(R_2Sn)_2Cl_2 + 2HCl \rightarrow 2R_2SnCl_2 + H_2.$$

Other workers[61], however, assign the one-electron process (8) followed by dimerisation by (9) merely to reduction of the trialkylhalogenotin (incidentally, hexaphenylditin is formed[108] on the cathode during the electrolysis of triphenyltin chloride), whereas complete reduction of butyltrichlorotin and dibutyldichlorotin has been regarded[99] as involving respectively three and two electrons. Two-electron reduction of a dialkyldichlorotin has been assumed also in other investigations[94,100,109]. We shall now examine the behaviour of individual organotin compounds.

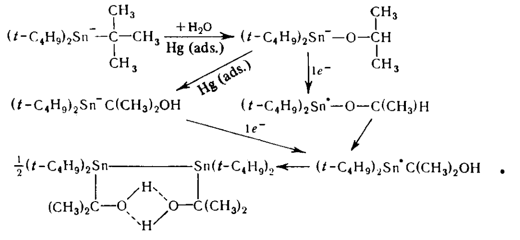
Trimethylchlorotin. In aqueous solutions two one-electron waves are obtained, whose heights are independent of pH, whereas the half-wave potentials become more negative with increase in pH (that of the second wave only in strongly alkaline medium).[103] An adsorption prewave precedes the second wave. With increase in depolariser concentration in an unbuffered medium the first wave divides into two steps, the first of which corresponds to reduction of the cationic form of the substance, and the second to that of trimethyltin hydroxide, which dissociates very slowly. The first wave represents formation of free radicals $(CH_3)_3Sn\cdot$, which dimerise to the water-insoluble hexamethylditin (the latter remains unreduced at a mercury electrode in oxolan up to −2.7 V). The second wave[103] is due to reduction of the radical to the anion $(CH_3)_3Sn^-$ (which then adds a proton), not to reduction of hexamethylditin; a similar process is suggested for the second wave in the reduction of triphenyltin chloride[87].

Di-t-butyltin. Very dilute solutions of the depolariser $(C_4H_9)_2Sn^{2+}$ in aqueous perchloric acid give polarograms having one diffusion reduction wave with $E_{\frac{1}{2}} = -0.55$ V, which is reversible and independent of pH.[110] Addition to the solution of increasing quantities of chloride ions shifts the wave to more negative potentials, divides it into two, and diminishes its height, conferring on it a kinetic character, and in 5 M hydrochloric acid almost completely eliminating the wave owing to the formation of a series of complexes. Studies have been made of complex formation also in buffered acetate, carbonate, and ammonium chloride solutions. Millimolar solutions of d-t-butyltin exhibit an adsorption prewave and two one-electron waves; the first stage involves formation of free radicals, which give dimeric products. The polarograms are greatly distorted by adsorption of the depolariser and especially of the electrode products. The presence of two t-butyl groups attached to tin facilitates transfer of the first electron and hinders that of the second electron in comparison with the diethyl or dimethyl derivatives, as well as stabilising considerably the four-coordinate state of tin[110].

t-Butyldiethyltin halides. With acid supporting electrolytes in 20% ethanol these give a reversible one-electron wave with an adsorption prewave; for the wave $E_{\frac{1}{2}} \simeq -1.1$ V (s.c.e.) at pH 4.6. With rise in pH the wave becomes less reversible and shifts to more cathodic potentials; a second, irreversible wave appears, lower than the first. In 1.0 *N* caustic soda the half-wave potentials are −1.45 and −1.70 V.[111] Preparative electrolysis shows that at the potential of the first wave the radicals formed dimerised to di-t-butyltetraethylditin. The same product occurs also at the potential of the second wave: the butyldiethylstannane $C_4H_9SnH(C_2H_5)_2$ formed in the second stage of the process probably reacts partly with the initial depolariser to give the dimer.

Di-t-butylethyltin bromide. The polarograms in acid solutions containing 20% of ethanol show two cathodic waves (half-wave potentials −1.05 and −1.45 V (s.c.e.) at pH 4.6) preceded by an adsorption prewave. The first, diffusion wave is reversible and corresponds to the transfer of one electron. The character of the second wave has not been established; the wave disappears on introduction of a surface-active substance into the solution. One one-electron wave occurs in alkaline medium, with $E_{\frac{1}{2}} = -1.55$ V in 1 *N* caustic soda. The waves are distorted by strong adsorption of the initial substance and the products, so that their form varies with increase in the depolariser concentration. Electrolysis yields tetra-t-butyldiethylditin.

Tri-t-butyltin. The behaviour of the cation differs appreciably[112] from that of mono- and di-t-butyl derivatives. A reversible main wave ($E_{\frac{1}{2}} = -0.6$ V at pH 1.9) and an adsorption prewave are found in acid solutions in 20% methanol. The limiting current is partly kinetic in character, although coulometric determination indicates a one-electron wave. When the solution is allowed to stand over mercury, the wave slowly diminishes, and at about −1.1 V a new wave grows to the one-electron level. Three waves are observed in alkaline medium: the sum of the first two corresponds to the transfer of one electron, and the height of the third wave also corresponds to such a process. Electrocapillary curves indicate strong adsorption of the initial depolariser and of the reaction products. Study by infrared and nuclear magnetic resonance spectroscopy of the products of preparative electrolysis suggests a general scheme involving comparatively rapid reaction between water and the depolariser adsorbed on the electrode, with elimination of a methyl group as methane and formation of an oxygen bridge; the product, which gives a wave having $E_{\frac{1}{2}} = -0.6$ V at pH 1.9, rearranges slowly in the adsorbed state to give the compound (wave with $E_{\frac{1}{2}} = -1.1$ V):



The half-wave potentials become in general more negative with increase in the number of alkyl groups attached to tin[92,95]: no reduction waves could be observed with tetra-alkyltins[109]. With increase in the length of the alkyl substituents the half-wave potentials of the reduction waves of organotin salts become less negative[92].

Butyltrichlorotin, dibutyldichlorotin, and tributylchlorotin. These compounds have been studied also by a.c. polarography[104]. Their adsorbability on the mercury electrode increases with the number of butyl groups. Tributylchlorotin has been investigated in greatest detail; the product of its reduction on the first wave is adsorbed far more strongly than is the initial depolariser, and the second reduction step gives an unadsorbable product. The height of the peak corresponding to the second stage of reduction increases sharply with rise in temperature, which confirms its kinetic nature. The electrochemical reaction at the second stage is irreversible, and the presence of a peak on the a.c. polarograms is attributed to change in the capacity of the double layer caused by reduction of a surface-active intermediate to an inactive end-product[104]. On the addition of propan-2-ol to the aqueous solution the peak height corresponding to the first wave becomes somewhat lower, whereas the peak corresponding to the second stage of reduction shifts abruptly to more cathodic potentials without significant change in height. It is interesting that the peak potential corresponding to desorption of propan-2-ol, located in front of the peak of the second wave, varies in almost the same way. In the presence of tributylchlorotin this desorption peak drops sharply, which is attributed to competitive adsorption of two substances; the effect increases with rise in temperature.

Aquodiethyltin. Voltammetry with a linearly varying potential shows that $(C_2H_5)_2Sn^{2+}.nH_2O$ gives on reduction extremely short-lived diethyltin biradicals, which are rapidly polymerised. The lower polymers can be oxidised anodically to the initial aquodiethyltin; oxidation of the higher polymers is accompanied by loss of some of the ethyl groups[113].

Triphenyltin. With tetrabutylammonium perchlorate in dimethoxyethane the chloride gives two waves[89], the first of which (one electron, $E_{\frac{1}{2}} \simeq -1.6$ V) corresponds to the formation of radicals that are rapidly converted into a dimer, whereas the second wave, which develops at extremely negative potentials, corresponds to reduction of the dimer (hexaphenylditin) to triphenyltin anions. In aqueous solution triphenyltin fluoride gives one irreversible one-electron wave representing reduction to hexaphenylditin, which is strongly adsorbed on the electrode[101].

The most detailed study has been made[102] of the behaviour of triphenyltin (acetate and hydroxide) in buffered solutions prepared in 50 vol.% ethanol. The polarograms contain three waves over a wide pH range: the heights of the first two waves are independent of pH; the third wave becomes visible at pH 4.75, reaches its maximum height at pH 7.3, and then falls along a kind of dissociation curve with further increase in pH. The half-wave potentials of first and second waves become more negative with rise in pH (in neutral and alkaline solutions $\Delta E_{\frac{1}{2}}/\Delta pH \simeq -60$ mV), their values at pH 7 being respectively −0.62 and −0.90 V (s.c.e.); that of the third wave is independent of pH ($E_{\frac{1}{2}} = -1.35$ V). On introduction of a tetrabutylammonium salt into the solution the third wave disappears, and the second becomes more extended. The first wave was shown to be an adsorption prewave; the total height of the first two waves corresponds to a one-electron diffusion current. The second wave is reversible in character, and the third irreversible. At high depolariser concentrations the heights of the second and third waves cease to increase with concentration. The first stage involves formation of the strongly adsorbable triphenyltin radical, which is either dimerised to electrochemically inactive hexaphenylditin or reduced further (the third wave) to the triphenyltin anion (after electrolysis at the potentials of the limiting-current plateau of the third wave an anodic wave with $E_{\frac{1}{2}} = -0.4$ V appears on the polarograms of the solution, and this corresponds to oxidation of triphenylstannane $(C_6H_5)_3SnH$ to the initial triphenyltin cation; no anodic wave appears after electrolysis at the potential of the second wave).

A method has been suggested[102] for determining microquantities (down to 10^{-8} M) of triphenyltin by the accumulation of adsorbed radicals by preliminary electrolysis of the test solution at a rotating mercury-coated platinum wire (at −1.0 V (s.c.e.) for 2 min) followed by anodic oxidation of the adsorbed radicals. With increase in time of pre-electrolysis or rise in concentration of the initial compound the height of the anodic peak ceases to increase, probably owing to dimerisation of some of the triphenyltin radicals to inactive hexaphenylditin; dimerisation is not observed at low surface concentrations of the radicals.

Hexaphenylditin. In dimethoxyethane this gives a two-electron wave at −2.9 V (relative to a 1 mM $AgClO_4$/Ag electrode), corresponding to formation of triphenyltin anions[87]. In aqueous–alcoholic medium, however, hexaphenylditin is electrochemically inactive[102].

Oxygen-containing organotin compounds. Trialkylstannyl methacrylates and ethers $R_3SnOSnR_3$ ($R = C_2H_5$, C_4H_9) in buffered aqueous solutions give two cathodic waves having half-wave potentials lying between −1.40 and −1.50 and between −1.74 and −1.78 V (s.c.e.) almost independent of the nature of the compounds, which is probably explained by their ready hydrolysis, e.g.

$$(C_2H_5)_3SnOSn(C_2H_5)_3 + H_2O \rightarrow 2(C_2H_5)_3SnOH) .$$

The first wave is rather more negative with ethyl than with butyl[114].

A polarographic method developed[115] for determining extremely small quantities (down to 3.4×10^{-7} M) of organotin compounds used as fungicides involves electrolysing the test solution in 12% hydrochloric acid at a suspended mercury drop cathode at −0.8 V (s.c.e.) for 5 min. The anodic current–potential curve for dissolution of tin from the amalgam is then recorded (rate of variation of potential 0.6 V min^{-1}), and the concentration of the organotin compound in the initial solution is calculated from the height of the peak. The method has been tested on benzyltin trichloride, octyltin trichloride, and dibenzyltin dichloride, as well as on benzylstannic acid.

Organolead compounds. One of the earliest studies[89] recorded polarograms for triethyl-lead chloride in aqueous potassium chloride. One-electron transfer was assumed to yield a triethyl-lead radical.

Aquodiethyl-lead. This species $(C_2H_5)_2Pb^{2+}.nH_2O$ is reduced[116] with the transfer of two electrons to biradicals, which partly disproportionate

$$2\,(C_2H_5)_2Pb^{\cdot\cdot} \rightarrow (C_2H_5)_4Pb + Pb^0$$

(this is favoured by increasing the concentration of the starting material), while the rest react with mercury

$$(C_2H_5)_2Pb^{\cdot\cdot} + Hg^0 \rightarrow (C_2H_5)_2Hg + Pb^0.$$

Trialkyl-lead bromides. These compounds have been studied in 30% isopropyl alcohol[117]. Triethyl-lead bromide gives two waves, the first ($E_{\frac{1}{2}} \simeq -0.7$ V) corresponding to the transfer of one electron followed by dimerisation of the resulting radicals to hexaethyldilead. With increase in the depolariser concentration this wave is split, the first step appearing as an adsorption prewave. The second wave on the polarograms of triethyl-lead bromide, with $E_{\frac{1}{2}} \simeq -1.35$ V (s.c.e.), forms a hump, and was attributed[117] not to the reduction of hexaethyldilead but to an unestablished process involving the initial compound. A detailed study was made[109] of the behaviour of trialkyl-lead chlorides.

Triethyl-lead hydroxide. In buffered aqueous solutions this compound gives two waves independent of pH, with half-wave potentials of −0.73 and −1.50 V (s.c.e.).[118]

Hexaethyldilead. A sharp wave is obtained[119] in anhydrous ethanol with tetraethylammonium iodide as supporting electrolyte (half-wave potential lying between −1.8 and −2.0 V relative to the mercury at the base of the cell). This compound can be determined polarographically as an impurity in tetraethyl-lead, which is polarographically inactive[109].

Phenyl-lead triacetate. Three one-electron diffusion waves, with respective half-wave potentials +0.1, −0.4, and −0.8 V (s.c.e.), are obtained[120] in 20% aqueous methanol in acid medium. A slight prewave occurs at −0.9 V, owing to the increase in the capacitive current resulting from desorption of reaction products. The first two waves are reversible, and the third is irreversible. After electrolysis at the plateau potentials of first and second waves diphenylmercury and bivalent lead were obtained, resulting from slow breakdown of products—$C_6H_5Pb(COO)_2^{\cdot}$ and $C_6H_5Pb(COO)^{\cdot\cdot}$ respectively—formed on the electrode; the kinetics of the breakdown of these radicals was studied. After electrolysis at the potential of the third wave only traces of diphenylmercury were found. When the solutions had stood for a few days, the first wave had diminished and divided, while the second wave had also split, this being explained by the replacement of acetate by hydroxyl groups. The products of electrolysis of the solutions after standing included not only diphenylmercury and Pb^{2+} but also phenol and metallic lead, formed by the reaction

$$C_6H_5Pb^{2+} + H_2O \rightarrow C_6H_5OH + H^+ + \frac{1}{2}(Pb^0 + Pb^{2+}).$$

Diphenyl-lead diacetate. In buffered acid and strongly alkaline solutions containing 20% of methanol this compound gives[121] an anodic oxidation wave, two two-electron reduction waves, and a prewave, which become more negative with increase in the depolariser concentration and with rise in pH (the substance is very sparingly soluble over the pH range 5–12). Owing to variation in the diffusion coefficient the waves are rather lower in alkaline than in acid medium. At a concentration of ~ 1 mM in 1 M perchloric acid the half-wave potentials are ~ +0.1 (anodic), −0.10 (prewave), −0.40, and −0.53 V (s.c.e.). Diphenyl-lead diacetate reacts comparatively rapidly with a mercury electrode ($k = 1.55 \times 10^{-4}$ cm s^{-1}) to form diphenylmercury and Pb^{2+}, so that preparative electrolysis cannot be accomplished at a mercury cathode. An extremely unstable diphenyl-lead biradical is assumed to be formed on the first wave, and to undergo rapid dismutation to hexaphenyldilead and metallic lead (Pb^0), and also reaction with mercury to yield diphenylmercury and metallic lead. On the second reduction wave the biradical gives benzene and metallic lead[121].

Triphenyl-lead hydroxide. In buffered solutions in 20% methanol reduction takes place in two stages, whose corresponding waves are preceded by an adsorption prewave[121]. The total wave height corresponds to a diffusion process with the transfer of four electrons. For a 1 mM solution in 1 M perchloric acid the half-wave potentials are respectively −0.17 (prewave), −0.43, and −0.55 V (s.c.e.). With decrease in depolariser concentration the half-wave potential of the prewave becomes less negative, and that of the second wave more negative, while that of the first wave remains unchanged. With rise in pH the half-wave potential of the first wave remains unchanged to pH 9 and then becomes more negative, whereas that of the second wave becomes more negative to pH 5.5, and is independent of higher pH. The first wave corresponds to the transfer of one electron with formation of a triphenyl-lead radical, which reacts rapidly with mercury to give diphenylmercury and metallic lead. The main reduction products at the potential of the second wave are benzene and lead.

The anodic oxidation of triphenyl-lead hydroxide yields bivalent lead, diphenylmercury, and phenylmercury ions[121]. The polarograms are distorted by adsorption phenomena (especially strongly at high depolariser concentrations). The second wave exhibits hysteresis: waves obtained with forward and reverse variation of the polarising voltage do not coincide.

Triphenylchlorolead and diphenyldichlorolead. In dimethoxyethane these compounds react with mercury to give diphenylmercury and metallic lead[87], but the corresponding acetates do not react with mercury under the same conditions. Diphenyl-lead diacetate gives[87] two one-electron waves (half-wave potentials of −1.1 and −1.6 V relative to $Ag/AgClO_4$—1 mM in dimethoxyethane). Electrolysis at the limiting-current potential of the second wave gives a quantitative yield of diphenylmercury.

Triphenyl-lead acetate. On the first one-electron wave (−1.4 V) in dimethoxyethane this gives the triphenyl-lead radical, but electrolysis at the limiting current of this wave gave diphenylmercury, not hexaphenyldilead: i.e. reaction of these radicals with mercury is considerably more rapid than their dimerisation[87]. The second wave ($E_{\frac{1}{2}}$ = −2.2 V) corresponds to the transfer of two electrons to the radical (to give a triphenyl-lead anion). The ease of addition of an electron increases in the sequence of compounds of silicon → germanium → tin → lead[87].

Hexaphenyldilead. In dimethoxyethane a two-electron wave is obtained representing formation of the triphenyl-lead anion ($E_{\frac{1}{2}}$ = −2.0 V relative to 1.0 mM $AgClO_4/Ag$).[87] At a platinised platinum electrode in a mixture of methanol and benzene the $(C_6H_5)_6Pb_2/(C_6H_5)_3Pb^+$ system is reversible.[122]

VII. DERIVATIVES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

Trisubstituted phosphines. Only the triaryl derivatives undergo reduction when polarographed[123-125]. With 0.09 M tetraethylammonium iodide in dimethylformamide $E_{\frac{1}{2}}$ = −2.670 V (s.c.e.) for the reversible one-electron wave of triphenylphosphine. The primary product is the radical-anion[123-126]. Preparative electrolysis yields diphenylphosphine and benzene.

Benzyldiphenylphosphine. This gives a two-electron wave corresponding to detachment of the benzyl group. Reduction is facilitated appreciably by replacing the phenyl by naphthyl groups[125].

Triphenylarsine, triphenylstibine, and triphenylbismuthine. These give two-electron waves[123]. The half-wave potential for triphenylarsine in dimethylformamide is −2.790 V (aq. s.c.e.).[125]

Triphenylphosphine, diphenylphosphine, and phosphinoacetates. These compounds, especially the last group, cause the catalytic evolution of hydrogen. The catalytic waves are greatly enlarged by the addition of cobalt(II), cobalt(III), and nickel(II) salts, except to triphenylphosphine solutions. In the presence of cobalt(III) even unsubstituted phosphine PH_3 produces a catalytic hydrogen wave, which in acid solutions (pH 3–5) is visible even with 10^{-7} M phosphine[127].

Triarylphosphines, triarylarsines, and triarylstibines. Half-wave potentials have been determined for the oxidation of several of these compounds in 0.1 M lithium perchlorate in acetonitrile. Values obtained for the triphenyl derivatives were respectively 0.12, 0.43, and 0.46 V (at 25°C relative to aqueous saturated KCl–AgCl/Ag). The wave heights correspond to the transfer of one electron. Preparative anodic oxidation gave the product $[Hg(Ar_3X)_2](ClO_4)_2$, where X = P, As, Sb.[128]

Diphenyl-phosphinous, -arsinous, -stibinous, and -bismuthinous halides, acetates, and perchlorates. In dimethoxyethane these compounds give irreversible reduction waves[129]. Only one one-electron wave, with $E_{\frac{1}{2}}$ = −3.3 V (relative to 1 mM $AgClO_4/Ag$), is observed for diphenylphosphinous chloride[129]:

$$(C_6H_5)_2PCl + e \rightarrow Cl^- + [(C_6H_5)_2P]^{\cdot} \xrightarrow{\text{solvent}} (C_6H_5)_2PH.$$

Diphenylarsinous bromide gives two one-electron waves, with tetraphenyldiarsenic as intermediate[129]:

$$(C_6H_5)_2AsBr \xrightarrow{e} Br^- + \frac{1}{2}(C_6H_5)_2As{-}As(C_6H_5)_2 \xrightarrow{e} (C_6H_5)\,As^-$$

with half-wave potentials of −0.9 and −2.7 V (relative to 1 mM $AgClO_4/Ag$). Reduction occurs in the same way with diphenylstibinous iodide (−1.0 and −2.5 V) and with diphenylbismuthinous chloride (−1.0 and −2.3 V), but the diphenylbismuth anion is unstable and decomposes with the separation of metallic bismuth[129].

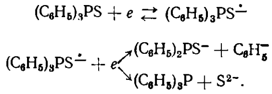
Phenylphosphonous and phenylarsonous dichlorides. In dimethoxyethane these compounds are reduced in a single two-electron stage:

$$C_6H_5PCl_2 + 2e \rightarrow 2Cl^- + [C_6H_5P]^{\cdot} \xrightarrow{\text{solvent}} C_6H_5PH_2.$$

The corresponding half-wave potentials are −2.5 and −0.9 V.[129]

Triarylphosphine oxides. In dimethylformamide these compounds give one reversible one-electron wave[125,126]. They are more easily reduced than are the corresponding phosphines. Thus the half-wave potential for triphenylphosphine oxide in dimethylformamide is −2.490 V (aq. s.c.e.)[125]. This oxide is strongly adsorbed from aqueous solution on a mercury electrode, and is therefore widely used to inhibit electrode processes[130]; it exhibits inhibiting properties, though less strongly, also in aqueous–methanolic[131] and methanolic[132] solutions. A detailed study has been made[132] of the effect of the nature and concentration of an inert salt and also the presence of a depolariser (azobenzene) on the adsorption of triphenylphosphine oxide from methanolic solution on a mercury electrode.

Triphenylphosphine sulphide. This gives three waves, with half-wave potentials −2.415, −2.530, and −2.700 V (aq. s.c.e.). The process corresponds to the scheme[125]



$$(C_6H_5)_3PS + e \rightleftarrows (C_6H_5)_3PS^{\dot{-}}$$

$$(C_6H_5)_3PS^{\dot{-}} + e \begin{array}{l} \nearrow (C_6H_5)_2PS^- + C_6H_5^- \\ \searrow (C_6H_5)_3P + S^{2-}. \end{array}$$

The third, small wave on the polarograms corresponds to reduction of triphenylphosphine.

Triphenylphosphine selenide. In dimethylformamide this gives one-electron waves with half-wave potentials of −2.145 and −2.690 V.[125]

Triarylarsine oxides and sulphides. These are reduced in dimethylformamide with the production of two waves. The half-wave potentials of the first wave are less negative than with the corresponding initial triarylarsines[125].

Aryldiethylarsine oxides. In dimethylformamide these give two-electron waves corresponding to detachment of the aryl group[133]. Addition of phenol to the solution causes the wave to grow and divide, so that two two-electron waves are produced in the presence of a fourfold to fivefold excess of phenol. The second wave then corresponds to reduction of the oxygen of the protonated species[133].

Quaternary phosphonium, arsonium, and stibonium salts. Many polarographic studies have been made of these compounds. A detailed summary will be found in Ref. 134, together with the polarographic characteristics of many phosphonium and arsonium salts in aqueous solution.

Tetraphenylphosphonium cation. Three reduction waves are obtained on the polarograms, the first corresponding to the transfer of one electron with the formation of triphenylphosphine and a phenyl radical, and the third to the reduction of phosphine[123], but the nature of the second wave was not established. Doubt has been cast on this mechanism[126]. In dimethylformamide the first wave is irreversible (according to results obtained with a Kalousek reversing switch)[126], but by analogy with the reduction of quaternary ammonium compounds[135], and on the basis of the slope of the lower part of the semi-logarithmic graph of the wave in aqueous medium[134,136], transfer of the first electron can be regarded as reversible or semi-reversible. From the inflexion in the upper part of the semi-logarithmic graph (Fig. 3 in Ref. 134) and the considerable shift in the half-wave potential to less negative values with increase in the depolariser concentration and the drop period of the electrode, it can then be supposed that electron transfer is followed by rapid bimolecular surface reaction (phosphines are strongly adsorbed on the electrode[127]) of the free radicals formed, yielding triphenylphosphine, phenyl radicals, and biphenyl, which was detected after electrolysis[124].

It has recently been shown[137] that minute quantities of hydroxide ions present in certain anhydrous media (if special measures are not taken to remove them) have a marked effect on the processes involved in the reduction of tetraphenylphosphonium salts. On polarography in dimethylformamide from which hydroxide ions (formed on storage in a glass vessel) have been specially removed the second wave on the polarogram of the tetraphenylphosphonium cation corresponds to reduction of triphenylphosphine oxide. If small quantities of hydroxide ions are present in the organic-solvent solution, the height of the second wave increases, and the limiting current of the first wave is smaller than the diffusion current corresponding to transfer of one electron, the number of electrons being less than unity by the concentration ratio $[OH^-]/[(C_6H_5)_4P^+]$ in the solution. This is due to occurrence of the very fast reactions

$$(C_6H_5)_4P^+ + OH^- \rightleftarrows (C_6H_5)_4POH, \qquad (11)$$

$$(C_6H_5)_4POH + OH^- \rightarrow (C_6H_5)_4PO^- + H_2O, \qquad (12)$$

followed by the comparatively slow process

$$(C_6H_5)_4PO^- \rightarrow (C_6H_5)_3PO + C_6H_5^-,$$

which under certain conditions (e.g. at very low temperatures) restricts the height of the second wave, and then the reaction

$$C_6H_5^- + H_2O \rightarrow C_6H_6 + OH^-.$$

Since dimethylformamide and acetonitrile usually contain a small quantity of water (0.1–0.2% and 0.4% respectively), the first stage of reduction (in the absence of hydroxide ions in the solution) takes place according to the scheme

$$(C_6H_5)_4P^+ + 2e + H_2O \rightarrow (C_6H_5)_3P + C_6H_6 + OH^-.$$

The hydroxide ions formed then react with a second molecule of the initial cation according to Eqn. (11), so that the height of the first wave corresponds formally to the transfer of one electron. In the preparative electrolysis of a tetraphenylphosphonium salt at the plateau potential of the first wave in dimethylformamide and acetonitrile not containing hydroxide ions, therefore, triphenylphosphine and its oxide are obtained in ~ 50% yield and benzene in 100% yield, which supports the above scheme. In conformity with this scheme the addition to dimethylformamide of formic acid, which suppresses reactions (11) and (12), raises the height of the first wave to a two-electron diffusion current. A similar but considerably smaller effect is produced by lithium ions (which combine with hydroxide ions) and also by water. The explanation for the latter[137] is that hydrated hydroxide ions are far less active than those solvated in dimethylformamide or acetonitrile.

The reversible character of transfer of the first electron to various phosphonium salts containing three phenyl groups has been shown in Ref. 138.

The half-wave potential of tetraphenylphosphonium in aqueous solution is −1.680 V (s.c.e.)[134], which becomes more negative on the successive replacement of phenyl by methyl or ethyl groups. Thus the potentials on passing from methyltriphenylphosphonium to trimethylphenylphosphonium are successively −1.862, −2.087, and −2.271 V.[134] When a phenyl group in tetraphenylphosphonium is replaced by other groups the half-wave reduction potentials become more negative in the sequence of substituents[136]

$$C_6H_5CH > (O)CH_3C_6H_4 > C(CH_3)_3 > C_6H_5 > C_2H_5 > CH_3.$$

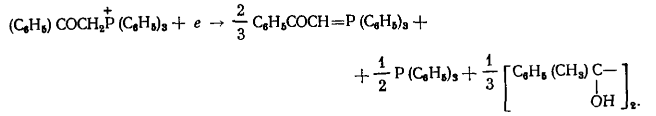
Diphenylmethyltriphenylphosphonium cation. With 0.1 M tetraethylammonium perchlorate in acetonitrile this gives two one-electron waves[139], corresponding to formation of an ylide and its reduction respectively. Addition of phenol (a proton donor) to the solution doubles the height of the first wave and suppresses the second. With tetrabutylammonium iodide as supporting electrolyte a third wave is observed, corresponding to triphenylphosphine. With the same supporting electrolyte these three waves are present on the polarogram obtained in dimethylformamide. The process can be represented by the general scheme

$$(C_6H_5)_2CH\overset{+}{P}(C_6H_5)_3 + e \rightarrow \frac{1}{2}(C_6H_5)_2C{=}P(C_6H_5)_3 + \frac{1}{2}(C_6H_5)_3P + \frac{1}{2}(C_6H_5)_2CH_2.$$

The appearance of an ylide is attributed[139] to abstraction of a proton from the initial cation on its interaction with a very strong base—the diphenylmethyl anion—formed on the electrode by transfer of an electron to the diphenylmethyl radical, which in turn appears together with triphenylphosphine as a result of comparatively slow decomposition of the primary electrode product—the free radical formed by reversible transfer of one electron to the initial cation. In the presence of a proton donor the usual two-electron rupture of a carbon–phosphorus bond takes place.

Benzyltriphenylphosphonium cation. This behaves similarly to the previous cation, giving two waves in acetonitrile with a tetra-alkylammonium salt as supporting electrolyte, and three waves in dimethylformamide or hexamethylphosphoramide with a tetrabutylammonium salt[139].

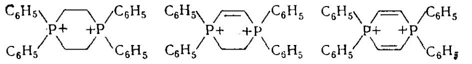
Phenacyltriphenylphosphonium cation. In acetonitrile this gives[139] three waves: the first corresponds to the transfer of one electron; the unusually low second wave was proved to represent reduction of the intermediate acetophenone (to "benzpinacone" [2,3-diphenylbutane-2,3-diol]; and the third wave, higher than the first, corresponds to reduction of the ylide and further reduction of acetophenone. The general scheme of the process is



$$(C_6H_5)\,COCH_2\overset{+}{P}(C_6H_5)_3 + e \rightarrow \frac{2}{3}\,C_6H_5COCH{=}P(C_6H_5)_3 + \frac{1}{2}\,P(C_6H_5)_3 + \frac{1}{3}\left[C_6H_5(CH_3)\underset{\displaystyle OH}{\underset{|}{C}}-\right]_2.$$

Polymethylenebistriphenylphosphonium salts. These compounds $[(C_6H_5)_3P[CH_2]_nP(C_6H_5)_3]Br_2$ having small values of *n* are reduced more easily than are the usual salts. With increase in *n* the half-wave potential becomes more negative, from −1.195 V when $n = 1$ to ~ −1.8 V when $n = 4-6$, after which it becomes more positive again[134].

1,1,4,4-Tetraphenyl-1,4-diphosphorinium salts. These salts, those containing the corresponding dihydro- and tetrahydro-rings



and numerous derivatives have been studied in dry dimethylformamide at a dropping mercury and a platinum microelectrode[140] with the use of 0.1 M tetraethylammonium perchlorate as inert electrolyte. The diphosphoniahexane derivative gives one two-electron wave with $E_{\frac{1}{2}} = -1.84$ V (s.c.e.) at a mercury electrode. The corresponding hexene and hexadiene derivatives are reduced considerably more readily: the first waves are reversible and correspond to the transfer of one electron forming radical-cations, with half-wave potentials respectively of −0.75 and −0.56 V. An especially detailed study has been made of a 2,5-di-t-butyl-1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexa-2,5-diene salt, which gives two one-electron waves ($E_{\frac{1}{2}} = -0.723$ and −1.08 V), the first being reversible and the second not. Addition of up to 10% of water to the dimethylformamide does not affect the height of the first wave, but in the presence of traces of perchloric acid the latter grows at the expense of the second wave, so that with increase in the acid concentration a single two-electron wave remains with $E_{\frac{1}{2}} = -0.675$ V.

The transfer of two electrons is regarded[140] as yielding a hitherto unknown compound—a diphosphabenzene derivative—which possesses basic properties and can be protonated at the carbon atoms; it resembles a diylide in character. Electrochemical reduction of the initial salt in aqueous-ethanolic medium gives a product without ring cleavage—a 1,4-diphosphoniacyclohexane derivative[141]—which is considered[140] to confirm the intermediate formation of diphosphabenzene. Substitution at positions 2 and 5 in the diphosphoniacyclohexadiene ring produces a change in half-wave potential in conformity with the inductive effect of the substituents (apart from di-t-butyl). Replacement of the *P*-phenyl groups by other substituents or substitution in the phenyl rings acts similarly. The waves are better defined at a platinum electrode, since they are distorted on mercury by adsorption phenomena[140].

Triphenyltriphosphine dianion. With tetrabutylammonium perchlorate in oxolan this species $(C_6H_5P)_3^{2-}$ gives an anodic oxidation wave at −1.4 V (relative to 0.1 *N* Ag^+/Ag), the product being probably[142] pentaphenylcyclopentaphosphine and hexaphenylcyclohexaphosphine $(C_6H_5P)_5$ and $(C_6H_5P)_6$. Mainly from the electrochemical behaviour of the triphenyltriphosphine dianion it was concluded that this compound has a linear structure, not the cyclic structure assumed earlier[143].

Pentaphenylcyclopentaphosphine and hexaphenylcyclohexaphosphine. With tetrabutylammonium perchlorate (concentration not indicated) in oxolan these compounds show the same electrochemical behaviour[142], giving at a dropping mercury electrode an irreversible two-electron reduction wave with $E_{\frac{1}{2}} = -2.62$ V (0.1 *N* Ag^+/Ag reference electrode) and a semi-logarithmic graph of slope corresponding to 63 mV. Cyclic voltammetry at a spherical platinum microelectrode gives a cathodic peak with $E_{p/2} = -2.8$ V, and on reversal of polarisation three anodic peaks with −1.9, −1.4, and −1.0 V, the second anodic peak being identical with the oxidation peak of the triphenyltriphosphine dianion. It is suggested that reduction yields an unstable dianion $(C_6H_5P)_n^{2-}$ ($n = 5,6$), which rapidly decomposes, so that the anodic peaks correspond to oxidation of the products formed.

Similar electrochemical behaviour is observed also with tetraphenylcyclotetraphosphine, as well as with alkyl derivatives of polycyclophosphines[144], for which the $E_{p/2}$ of the cathodic peak correlates well with the Taft σ-constants of the alkyl groups (the $E_{p/2}$ of the phenyl derivatives also lie on the straight line obtained).

Arsonium salts. These behave like phosphonium salts, but are more easily reduced, their half-wave potentials being ~ 0.3 V more positive than those of the corresponding phosphonium derivatives[134]. One or two reduction steps are observed depending on the nature of the substituents.

Hexaphenylhexa-arsine. Like the phosphorus analogue, $(C_6H_5As)_6$ on cyclic voltammetry at a platinum electrode gives a cathodic peak with $E_{p/2} = -2.8$ V, and on anodic polarisation three oxidation peaks with −2.0, −1.5, and −1.2 V.[142] Exhaustive electrochemical reduction yields a new substance, whose reduction gives $E_{p/2} = -3.0$ V, probably neutral diarsine. The corresponding diphosphines are electrochemically inactive.

Tetramethylstibonium. In aqueous solution the polarograms contain a single irreversible two-electron wave with $E_{\frac{1}{2}} = -1.490$ V (s.c.e.), corresponding to formation of trimethylstibine and methane[145].

Trimethylphenylstibonium, dimethyldiphenylstibonium, methyltriphenylstibonium, and tetraphenylstibonium. In aqueous media these give two one-electron diffusion waves[145]. The first wave corresponds to reversible electron transfer with formation of a tetrasubstituted stibine radical, which reacts rapidly with mercury to give a trisubstituted stibine and an organomercury radical, the latter disproportionating to a disubstituted organomercury derivative. The half-wave potential of the first wave has the respective values −1.195, −0.900, −0.710, and −0.635 V (s.c.e.) for the above compounds. The second wave is irreversible.

The half-wave potentials of both waves are independent of pH over the range studied (4–12). Electrolysis on the limiting-current plateau of both waves yields a trisubstituted stibine and a hydrocarbon (benzene or methane), but formation of the latter is not a consequence of reduction of the organomercury radical (as supposed[134] from the identity of the half-wave potentials for the second wave of tetraphenylstibonium and the phenylmercury ion). This follows from the simultaneous detachment of methyl and phenyl groups on electrolysis, in different ratios at the potentials of the first and second waves. In contrast to alkylaryl-phosphonium and -arsonium ions the nature of the group split off on the cathodic reduction of tetrasubstituted stibonium ions is determined by the stability not only of the resulting hydrocarbon radical but also of the stibine derivative[145]. The second wave corresponds to transfer of an electron and then also a proton to the tetrasubstituted stibine radical, to yield a trisubstituted stibine and a hydrocarbon.

The adsorbability of methylphenylstibonium ions on a mercury electrode is considerably enhanced with increase in the number of phenyl groups.

Preparative electrolysis of a tetraphenylstibonium solution at the potential of the first-wave plateau gave only triphenylstibine and diphenylmercury (neither benzene nor biphenyl was detected among the products). The second wave on the polarograms of tetraphenylstibonium corresponds to reduction of diphenylmercury formed in the first stage[146].

Tetratolylstibonium. In aqueous solution this gives two one-electron waves, the first of which is reversible[147].

Tetraphenylbismuth cation. Unpublished results indicate[145] two one-electron waves in aqueous solution.

Pentaphenylphosphorane. With 0.1 M tetrabutylammonium iodide in dimethylformamide this gives one irreversible wave[137]. The peak potential on voltammetry (with linear variation of potential) is −2.75 V (aq. s.c.e.).

Phosphoric esters. Only a capacitive cathodic spur appears on the $dE/dt = f(E)$ oscillopolarograms obtained in 1 M aqueous potassium chloride for the esters from trimethyl to triphenyl phosphates.

Trialkyl phosphites. These give an additional spur caused by the formation of compounds with mercury[148].

Tri-*p*-nitrophenyl phosphate. Of the five reduction waves the first represents an adsorption effect, the second is a diffusion wave with the transfer of two electrons, the third is kinetic, and the fourth and fifth waves are strongly distorted maxima, whose nature has not been established. On the second wave the dianion $[(NO_2C_6H_4O)_3PO]^{2-}$ is formed, and is slowly converted by interaction with the solvent into *pp'*-dinitrobiphenyl and nitrophenyl dihydrogen phosphate $NO_2C_6H_4OPO(OH)_2$.[149]

Di-*p*-nitrophenyl hydrogen phosphate. In dimethylformamide this ester $(NO_2C_6H_4O)_2POOH$ gives three waves. The second is a diffusion wave with the transfer of two electrons and formation of a dianion converted by reaction with the solvent into *pp'*-dinitrobiphenyl and phosphoric acid[150].

Phenyl- and *β*-styryl-phosphonic and -phosphinic esters. In dimethylformamide these give one or two one-electron cathodic waves, the first of which is reversible[126,151]. The styrylphosphonates are reduced more readily than styrene itself by almost 0.5 V. It is interesting that the half-wave potentials are almost the same for the styrylphosphonate and a styrylphosphinate (−1.45 and −1.81 compared with −1.45 and −1.85 V relative to mercury in 0.08 M tetraethylammonium iodide).[151]

Vinylphosphonic and divinylphosphinic esters. In dimethylformamide these compounds $CH_2:CH.PO(OC_2H_5)_2$ and $(CH_2:CH)_2POOC_2H_5$ have one-step two-electron reduction waves with respective half-wave potentials of −2.02 and −1.87 V (relative to mercury in 0.08 M tetraethylammonium iodide).[126]

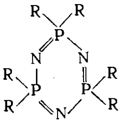
Diethyl aroylphosphonates. On reduction at a dropping mercury electrode in acetonitrile these esters $ArCO.PO(OC_2H_5)_2$ give diethyl phosphonates and benzoin. In the presence of benzoic acid diethyl *α*-hydroxyarylmethylphosphonates are formed[152].

Diethyl *α*-diazobenzylphosphonate. With 1 M lithium perchlorate in 20% aqueous dioxan this ester $C_6H_5.CN_2.PO(OC_2H_5)_2$ and its *para*-substituted derivatives give one irreversible two-electron diffusion wave ($E_{\frac{1}{2}} = -1.18$ V (s.c.e.) for the unsubstituted ester), corresponding to replacement of the diazo-group by two hydrogen atoms[153]. The corresponding potentials of the substituted derivatives vary in conformity with the Hammett equation containing the constant $\rho = +0.098$. Under the same conditions ethyl *α*-diazophenylacetate gives a wave having $E_{\frac{1}{2}} = -1.17$ V: i.e. the effect of the diethoxyphosphinyl group on reduction of the diazo-group is almost the same as that of the ethoxycarbonyl group[153].

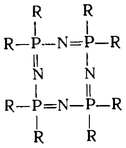
At a rotating platinum disc electrode the above phosphonates give one-electron diffusion waves, which with certain derivatives are reversible.

Acylphosphine oxides. In dimethylformamide and acetonitrile these compounds RCO.PORR′ acquire the first electron irreversibly when R = CH_3 and reversibly when R = C_6H_5.[154]

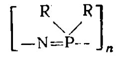
Organocyclophosphazines. Compounds having a six- or eight-membered ring (III) or (IV) or the polymeric linear structure (V)



(III)



(IV)



(V)

($n \simeq 15$; R = C_6H_5, OC_6H_5, OCH_2CF_3, etc.) are reduced in dimethylformamide in the presence of 0.1 M tetrabutylammonium iodide, giving a one-electron first wave followed, immediately before discharge of the supporting electrolyte, by another, very indistinct wave corresponding to transfer of a second electron[155]. The size of the ring is almost without effect on the half-wave potential of the first wave (with R = C_6H_5 structures (III) and (IV) have the values −2.65 and −2.67 V s.c.e.). Coulometric electrolysis of (III) at the limiting-current potential of the first wave showed complete regeneration of the depolariser: i.e. the first wave is catalytic in character. Cyclic voltammetry indicates the instability of the radical-anions formed on transfer of the first electron[155].

The present Review has given the principal information available on the polarographic behaviour of organoelementary compounds of non-transition elements. A brief summary of results for derivatives of transition metals can be found in the recently published Russian translation of the book by Mann and Barnes[156].

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Advances in Fluorine Calorimetry

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The development of a new area of thermochemistry (the calorimetry of fluorination reactions) is reviewed. The high reactivity of fluorine offers some important advantages over alternative reagents, but at the same time it introduces some experimental difficulties. We have attempted to generalise the practical problems of fluorine calorimetry by systematically examining a number of specific thermochemical investigations by the most widely adopted modification of the method: fluorine bomb calorimetry. Current developments and possible new applications are reviewed, and the basic experimental procedures and apparatus are described. 86 references.

CONTENTS

I. INTRODUCTION

The method known as "fluorine calorimetry" includes two main modifications, differing in the details of the calorimetric measurement. The first modification relies on combustion of the sample in fluorine within a calorimetric bomb ("fluorine bomb calorimetry"). This is the latest and most important development in the fundamental thermochemical procedure of bomb calorimetry. The second modification relies on combustion in fluorine with formation of a flame in a special flow-through calorimeter ("fluorine flame calorimetry"). Its applications are more limited, since it is assumed that only gaseous products are formed.

The term "fluorine calorimetry" includes all thermochemical studies of fluorination reactions, whether or not the fluorine is in the elemental state. The replacement of fluorine by a fluorine compound of comparable oxidising power (inert gas fluorides, oxygen fluorides, halogen fluorides) is a mere extension of the method without any fundamental difference.

Thermochemical studies of fluorination reactions were first reported[1] in the 1930's, but precise measurements of the heats of reactions were not attempted until approximately 1960. In 1959 Gross[2], of the Fulmer Research Institute in Great Britain, published the results of his calorimetric measurements of the heats of formation of SF_6(g) and TiF_4(c), obtained by burning sulphur or titanium in fluorine in a special glass bomb. Important contributions to the development of the fluorine bomb came from Hubbard and coworkers[3] of the Argonne National Laboratory, USA, and from Armstrong and coworkers[4] of the National Bureau of Standards, USA. These workers demonstrated the precision attainable by this method, they developed new apparatus for general application, and they proposed new combustion procedures. At the same time Armstrong developed and successfully applied the method of "fluorine flame calorimetry".

Work on reaction calorimetry by using fluorine in a bomb began in the Soviet Union in 1967 at the Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences and also at the High Temperatures Institute of the USSR Academy of Sciences.

Whereas the combustion method using fluorine in a bomb has been used successfully in several laboratories in the USA, Great Britain, West Germany, France, and the Soviet Union, the work using fluorine flames remains the prerogative of a single laboratory (the National Bureau of Standards in the USA). Partly because of its limited applications, and partly because of the lack of direct experience in our own laboratory, we have thought it preferable not to include a discussion of fluorine reaction calorimetry in flames in the present review.

There can no longer be any doubt that fluorine calorimetry offers entirely new possibilities in experimental thermochemistry, since it allows the study of reactions involving substances too unreactive to be investigated by other methods. From the thermochemical point of view reactions with fluorine are more attractive than reactions with oxygen because of the higher oxidising power of elemental fluorine. They are more exothermic and more readily initiated under the conditions of a calorimetric experiment. Fluorides tend to have more definite compositions than oxides. In the great majority of cases combustion in a bomb under a high pressure of fluorine gives the higher fluoride, whereas calorimetric combustion in oxygen can yield crystalline or glassy protective oxide films which make the reaction diffusion-limited and can lead to products of indefinite composition such as mixtures of oxides or phases of variable composition. Effects of this type are responsible for the low precision of oxygen bomb measurements on compounds containing silicon, boron, germanium, and some multivalent transition elements.

Fluorides are "low-temperature" compounds compared with oxides. Most of the higher fluorides have a significant vapour pressure at normal temperature. The presence of gaseous or distillable products in the calorimetric bomb makes their identification and analysis much simpler.

For these reasons reliable values of the standard heat of formation of many compounds were not available before the advent of fluorine calorimetry. Precise measurements of the heats of formation of fluorides by the direct thermochemical method (reaction between the element and fluorine) are important in their own right because of the major role played by these compounds in chemistry, chemical technology, and industry.

The compounds which have been studied by fluorine calorimetry up to the time of writing are listed in the Table. It can be seen that combustion in a fluorine bomb is the main form of the fluorine calorimetry method, having been used successfully to measure the heats of formation of higher and lower fluorides, oxides, refractories, and some other compounds. After the fluorides, the most important group of compounds in the list includes those of silicon (SiO_2, SiC), germanium (GeO_2, GeS), and boron (Zr, Hf, Nb, and Ta borides, and B_2O_3), i.e. the compounds which cannot be studied accurately by oxygen combustion for the reasons stated above. The bomb combustion methods in which fluorine is replaced by other fluorinating agents are likely to be developed further.

Compounds whose heats of formation have been studied by fluorine calorimetry*.

No	Compound	Reference	Notes
	Reactions with fluorine in a bomb calorimeter		
1	$SF_6(g)$	2. 5, 6, 7	synthesis from the elements
2	$TiF_4(c)$	2, 8	
3	$ZrF_4(c)$	9	
4	$MoF_6(g)$	10	
5	$BF_3(g)$	11, 12, 13, 14, 15	
6	$HfF_4(c)$	8	
7	$UF_6(g)$; $UF_6(c)$	16, 17	
8	$SiF_4(g)$	18	
9	$CdF_2(c)$	19	
10	HF(l)	20	
11	$ZnF_2(c)$	21	
12	$MgF_2(c)$	22	
13	$AlF_3(c)$	23, 24	
14	$NbF_5(c)$; $TaF_5(c)$	25	
15	$YF_3(c)$	26	
16	$BeF_2(c)$	27, 28	
17	$RuF_5(c)$	29	
18	$AsF_5(g)$	30	
19	$SeF_6(g)$; $TeF_6(g)$	5	
20	$WF_6(g)$	31, 6, 32, 33	
21	$PF_5(g)$	34, 35, 36	
22	$NiF_2(c)$	37	
23	$CF_4(g)$	38, 39, 40	
24	$GeF_4(g)$	41, 42, 43	
25	$VF_5(c)$	44	
26	$CuF_2(c)$	33	
27	$1/n(C_2F_4)_n(c)$	23, 38, 40	combustion of lower fluorides to higher fluorides
28	$UF_3(c)$; $UF_4(c)$	17	
29	$GeF_2(c)$	45	
30	$WF_5(c)$	6	
31	$PF_3(g)$	46	
32	$SiO_2(c)$	18	reaction of oxide with fluorine
33	$GeO_2(c)$	41	
34	$B_2O_3(c)$	47	
35	AlB_2; AlB_{12}	48	reaction with refractory compounds
36	BN	15, 49	
37	ZrB_2; HfB_2	50	
38	NbB_2; TaB_2	51	
39	B_4C	52	
40	UB_2	53	
41	BP	36	
42	SiC	54	
43	GeS	55	
44	MoS_2	56	
45	Si_3N_4; GaN	57	
46	W_2B	58	
47	$NSF_3(g)$)	59	other compounds
	Reactions with other fluorinated oxidising agents in a bomb calorimeter		
48	$OF_2(g)$	60, 61	reaction with H_2
49	$NF_3(g)$	62	reaction with elemental sulphur
50	ClF(g)	63	reaction with H_2
	$ClF_3(g)$	»	
	$ClF_5(g)$	63, 64	
51	$ClF_5(l)$	64	ditto
52	$XeF_2(c)$	65	reaction with PF_3
	$XeF_4(c)$	»	
	$XeF_6(c)$	»	
	Reactions in flames in a flow calorimeter		
53	HF(g)	4	reaction of fluorine with H_2 and NH_3
54	$OF_2(g)$; HF (soln.)	66	reaction with H_2 followed by dissolution in water
55	$ClF_3(g)$	67	
56	ClF(g); $ClF_5(g)$	67, 68	ditto

* Compounds within each group are listed in order of appearance of the first publication. The basis of the classification is stated in the Notes.

The use of fluorine compounds such as the inert gas fluorides often brings a number of advantages. However their exploitation requires some preliminary work: in particular, accurate measurements of the heats of formation of these fluorides, and the development of methods for causing combustion and for analysing the combustion products. Fluorine flame calorimetry is useful for determining the heats of formation of some reactive gaseous fluorides.

II. SPECIAL FEATURES OF COMBUSTION IN FLUORINE IN A CALORIMETRIC BOMB

The high reactivity of fluorine and fluorides can induce various side reactions, leading to systematic errors in the measurement of the heat of the main reaction. One of the main features of fluorine calorimetry is the need to develop procedures for avoiding these side reactions or accurately correcting for them. We shall discuss this aspect in detail for the special case of combustion in fluorine within a calorimetric bomb.

Obviously, one of the main problems is to avoid side reactions involving fluorine. The fluorine is present in the bomb at a relatively high pressure, and it can interact with the container material. Corrosion of the apparatus during the measurement can be a serious problem†, but it can be minimised to a level which produces a negligible error (thermal effect of the corrosion reaction less than 0.01% of the thermal effect of the main reaction)[10,11] by suitable choice of materials and methods of passivation, and also by careful design and operation of the calorimetric bomb. Heavy corrosion of the other parts of the apparatus (connecting tubes, taps, storage vessels) is also unacceptable because the fluorine can be contaminated with oxygen and other impurities if it is allowed to come into contact with an oxidised metal surface. On the other hand, metal surfaces covered by a passivating film of fluoride can show increased adsorption and a tendency to hydrolysis. A passivating fluoride film on the inner wall of the calorimetric bomb may interact with the products of the main reaction.

The experimental substance can begin to react with the fluorine in the bomb even before the start of the main period of the calorimetric experiment. Hence the thermochemical experiment must be supplemented by tests for this interaction, and if necessary the bomb must be provided with two compartments or other means of isolating the reactants. All these precautions relate, to a greater or lesser extent, to apparatus design. Accurate measurements of the heat of fluorination reactions cannot be attempted without special fluorine-handling equipment, made of the smallest number of fluorine-resistant materials, and operated with careful attention to the special requirements of this procedure.

Let us now consider the possibility of side reactions with impurities in the fluorine used for the calorimetric experiment. A survey of all the papers published on fluorine bomb calorimetry shows that the purity of the fluorine used by different authors varies in the range 99.0–99.99 vol.%. The earlier workers[9,10,35] tended, as a rule, to purify their fluorine by low-temperature distillation[69]. By using laborious procedures with distillation apparatus operated under laboratory conditions they were able to prepare very pure fluorine containing only a few hundredths of one per cent of oxygen and nitrogen as the main impurities[9].

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†Some measurements[66,68] by fluorine flame calorimetry have had to be corrected for the corrosion of the apparatus in OF_2 and ClF_3. In the ClF_3 experiment[68] the correction amounted to 0.33% of the measured thermal effect of the $ClF_3 + H_2$ reaction.

At the same time, Domalski and Armstrong[23] measured the heat of formation of AlF_3 with fluorine containing 1 vol. % of impurities (0.9% O_2, 0.08% N_2, 0.01% CO_2, traces of SiF_4, HF, and fluorocarbons). Later the same workers[70] gave detailed information on the impurity content of two samples of commercial fluorine (99.40 vol. % F_2 and 99.79 vol. % F_2) which they used for calorimetric combustions of aluminium borides and graphite. Thus, both specially purified fluorine and fluorine of commercial purity have been used in fluorine calorimetry. The tendency to use the latter is explained by recent improvements in industrial processes, which now enable a level of purity in excess of 99.5% to be reliably obtained in commercial fluorine. However, the spectrum of impurities in the material is not constant, and depends on many factors including the grade of the starting material and unavoidable process variations. We must therefore consider the extent to which various possible impurities could take part in side reactions during the calorimetric experiment.

There is general agreement[69-72] that the commonest impurities in fluorine are O_2, N_2, HF, oxygen fluorides, fluorocarbons, CO_2, SiF_4, NF_3, SF_6, SO_2F_2, and Ar. An analysis[68,69] of many samples of commercial fluorine suggests that the predominant impurities are O_2, N_2, SiF_4, and CO_2. For example, the combined amount of these impurities in two fluorine samples containing 0.60 and 0.21 vol. % of total impurity was found to be[70] >98% of the total. Although the most reactive impurities (oxygen fluorides and hydrogen fluoride) are not usually detected, it cannot be assumed that their concentration is so low as to guarantee freedom from side reactions, since the occurrence (or otherwise) of these reactions depends also on the chemical properties of the substance under study. For example, according to Leonidov and coworkers[32] tungsten reacts spontaneously in the bomb if the fluorine contains ~1 vol. % of oxygen impurity. Spontaneous reaction was not observed when the oxygen content was decreased to 0.1 vol. %. Similar effects may occur with other impurities in the fluorine, which may therefore affect the result to different extents depending on the use to which the fluorine is put.

Thus the required level of purity of the fluorine may vary according to the nature of the impurities and that of the experimental substance. It is not enough to have access to high-purity fluorine: a qualitative and quantitative analysis of the impurities is essential, both before and after the calorimetric experiment‡. This presupposes that a high-precision method of analysis of fluorine and of the impurities in the gas is available. The need exists even if fluorine of the highest purity is used (such as fluorine purified by low-temperature distillation). Thus, Gillardean and coworkers[73] have shown that even very low (> 0.1 vol. %) concentrations of oxygen in the fluorine can affect the mechanism of fluorination of metallic copper.

It follows that an accurate method of fluorine analysis must be available, in addition to suitable calorimetric apparatus, in any laboratory attempting to use fluorine calorimetry.

The third essential precaution to avoid systematic errors through possible side reactions in the calorimetric bomb is a proper choice of the conditions under which the sample is burned in fluorine (combustion procedure).

The best combustion conditions in "oxygen" bomb calorimetry are those for which the oxidation reaction proceeds with a full yield of products of well-defined composition. When the sample is burned in a fluorine bomb calorimeter there is an additional requirement: freedom from side reactions by the fluorine or by the resulting fluorides. This requirement can introduce serious difficulties into the choice of the optimum method of combustion in fluorine. The combustion conditions cannot be really satisfactory unless the initial pressure of fluorine is as low as possible, since the probability of side reactions increases rapidly with pressure. The choice of optimum conditions for combustion in fluorine is further complicated by the likelihood of spontaneous reaction. Because of all these difficulties, we shall attempt a general discussion of the special features of calorimetric combustion in fluorine in relation to the type of sample used, and we shall make some general recommendations on the best experimental conditions in each case.

Thus, the following sections will deal in detail with the analytical determination of fluorine and its impurities, with non-standard apparatus for calorimetric work with fluorine, and with combustion methods for various substances. Since the measurement procedure, the design of the calorimeter, and the calculation of the calorimetric results do not differ in any way from those used, for example, in calorimetric combustions in oxygen[74], we shall not dwell on these problems in the present review§.

III. FLUORINE ANALYSIS

The mercury method, consisting in chemically absorbing the fluorine in metallic mercury and measuring the volume of residual gases, is generally used for fluorine analysis in calorimetric work. Klyuev[81] has given a full review of all the published work on the mercury method. This is undoubtedly the most accurate chemical method of analysis of high-purity fluorine. It is relatively simple and convenient under laboratory conditions. The method is applied in a variety of forms, differing in the method of measuring the volume of residual gas, in the design of the apparatus, and in the attainable precision. We shall briefly outline the published work on the application of this method to fluorine calorimetry.

Armstrong and Jessup[4] analysed fluorine of 97–99 vol.% purity by the following procedure. A quartz vessel 50 cm^3 in volume containing 1–2 cm^3 of pure mercury was evacuated to a pressure of 0.01 mmHg, and filled with fluorine at atmospheric pressure through a special micro-valve. The valve was shut, the vessel was disconnected from the gas lines, and it was manually shaken for 10–15 min.

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‡As well as measuring the concentration of impurities in the fluorine before and after the calorimetric experiment, special experiments are necessary to prove that there has been no reaction of the main sample with the various impurity components. Thus Domalski and Armstrong[23], having used fluorine containing 0.9 vol.% of oxygen for the calorimetric combustion of aluminium, also burned a sample of aluminium in an equimolar mixture of fluorine and oxygen to show that aluminium oxide is not formed even at that concentration of oxygen.

§Most of the calorimetric measurements of fluorine bomb calorimetry (see Table) were carried out in standard water calorimeters with an isothermal enclosure (with the exception of the work of Gross and coworkers[2,13,15,35,36,41], Hayman[17], and Schröder[6]). The only non-standard component of the calorimetric system was the bomb itself.

Complete absorption of the fluorine was judged from the cooling of the vessel and from the change in colour of the mercury surface. The residual pressure was measured with a U-tube manometer filled with fluorocarbon oil. The manometer reading was corrected for the expansion of the gases into the auxiliary volumes (manometer limb, connecting tube) and the volume of the residual, non-absorbed gas was calculated. A reproducibility of 0.05% in a short series of measurements is claimed[4]. A similar procedure was used in calorimetric experiments by Stein and coworkers[69], Armstrong and coworkers[67,70], and Hubbard and coworkers[3]. Stein[69] describes an i.r. spectral method of estimating HF, OF_2, CF_4, C_2F_6, C_3F_8, NF_3, and CO_2 impurities in the residual gas. Domalski and Armstrong[70] reported some measurements of the impurity content of commercial fluorine samples (see above) by a mass spectrometric identification of the residual gas components. The same method was used to analyse fluorine of 99.95% purity, purified by low-temperature distillation[3]. Subsequently King and Armstrong[67], and also Pervov and coworkers[75], used gas chromatography to determine oxygen and nitrogen impurities in the gas which was not absorbed by mercury.

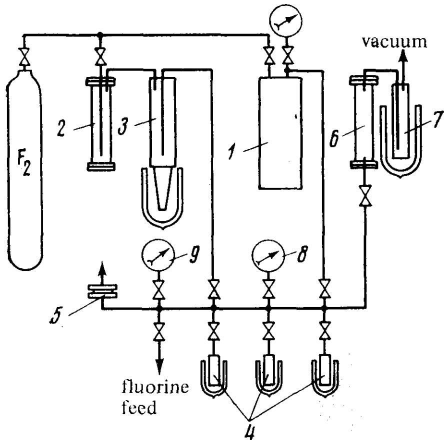

Figure 1. Apparatus for fluorine purification: *1*) storage vessel, *2*) granulated NaF absorber for removing HF, *3*) low-temperature condenser with nickel packing, *4*) receivers for fluorine condensation, *5*) pressure relieving valve, *6*) tube packed with metallic silicon for fluorine absorption, *7*) trap for SiF_4, *8*) manometer, *9*) vacuum gauge.

However, in spite of their good reproducibility (0.05–0.10%), many of the reported analytical results for fluorine[3,67,69,70] have doubtful precision. Most of the early work on the mercury method includes several sources of systematic error which affect the results of the fluorine analysis. For example, later workers[71,76] have identified the reaction between some impurities (HF, OF_2) and mercury as the main source of systematic error. According to Miller and Bigellow[77] the main contribution to the lack of precision comes from the pressure measurements (both the initial pressure of fluorine and the final pressure of the residual gases). A recent paper[75] suggests that the analytical results can be affected by the adsorption of impurities on the mercury fluoride, by temperature changes during the reaction between fluorine and mercury, and by the mixing conditions.

Pervov and coworkers[75] have made a thorough study of the effect of all these factors on the precision of the analysis of fluorine containing only oxygen and nitrogen impurities. They found that, because of the variability of the impurities in ordinary fluorine and of their chemical behaviour under the conditions of analysis by the mercury method, results of adequate precision can be obtained only if the analytical problem is simplified by a preliminary purification of the fluorine. They suggest a relatively simple method of purification, consisting in freezing out most of the impurities (except oxygen and nitrogen) in a flow-through trap at −170°. This procedure achieves two desirable ends: the reliability of the calorimetric results is improved by the use of purer fluorine, and the analytical data are more precise.

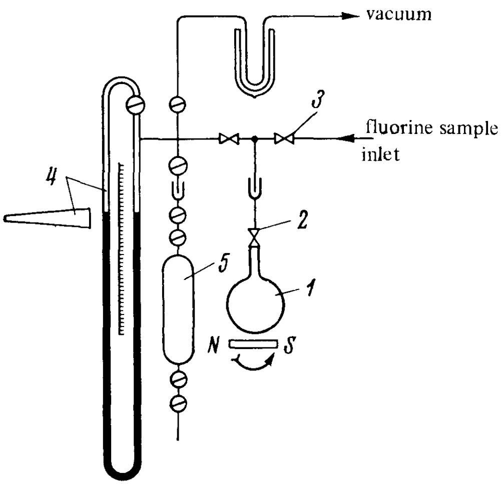

Figure 2. Fluorine analysis apparatus: *1*) flask, *2*) needle valve, *3*) tap, *4*) mercury manometer with cathetometer, *5*) gas burette for sampling residual gas.

The apparatus for removing impurities from the fluorine[75] except oxygen and nitrogen is shown in Fig. 1.

Fig. 2 shows an improved apparatus[75] for the analysis of the purified fluorine (>99.5 vol. % F_2) by the mercury method with a guaranteed precision. The total concentration of impurities is measured with a precision of 0.05 to 0.10 vol.%; identification is by mass spectrometric or gas chromatographic analysis of the residual gas. This form of the mercury method is ideally suited[4,75] to the analysis of high-purity fluorine (~99.9%), since in this case also the main impurities are oxygen and nitrogen[9], and there are no systematic errors from side reaction or adsorption of impurities. In either case the fluorine used in the calorimetric experiment can be analysed with a precision sufficient to give a reliable correction for the heat of the reaction with the oxygen and nitrogen impurities in the bomb, or alternatively to prove that the correction is unnecessary.

IV. APPARATUS

The equipment needed for fluorine bomb calorimetry includes the special calorimetric bombs¶ and apparatus for the preliminary purification and anslysis of the fluorine, for filling the bomb, and for sampling and separating the gaseous combustion products. Careful commissioning and operation of this specialised equipment is an essential prerequisite to the achievement of high precision in the measurement of heats of combustion in fluorine. A glass bomb for preliminary experiments on the optimisation of the conditions of combustion in fluorine should also be available because visual observations can be very valuable in this type of work†.

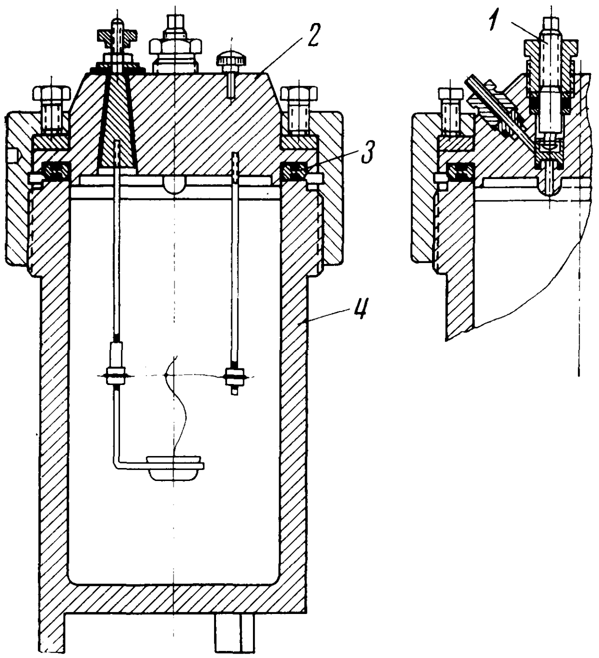

Figure 3. Single-chamber bomb calorimeter: *1*) valve, *2*) lid, *3*) seal, *4*) body.

The design of the calorimetric bomb must take account of a number of special requirements which are common to all fluorine-handling equipment. First and foremost, the bombs must be made of fluorine-resistant materials such as pure nickel, Monel metal, some high-alloy carbon-free steels of the Fe–Cr–Ni type, aluminium, gold, and Teflon (used to make sealing gaskets and partitions). Some types of ceramic can also be used (fluorite, fused alumina, and in some cases fused quartz[3,67]). Mechanical properties, operating conditions, and passivation regimes all have to be considered before finalising the choice of materials. For example, Teflon and quartz can ignite spontaneously in compressed fluorine at moderately high temperatures (50–100°). A reliable and simple operating procedure is another important requirement for equipment (including calorimeters) designed to handle fluorine under pressure.

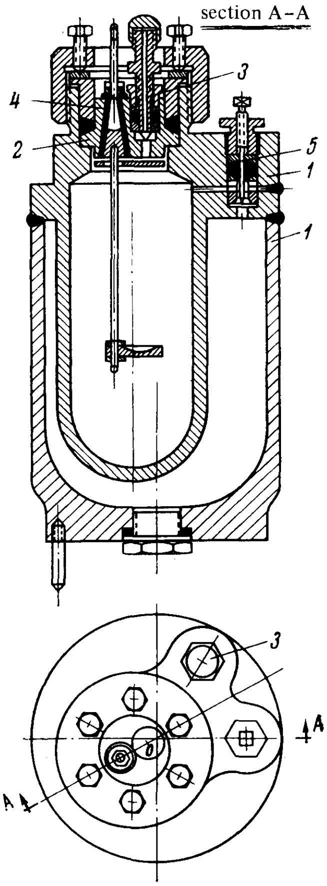

Figure 4. Double-chamber bomb calorimeter: *1*) body, *2*) lid, *3*) valve, *4*) electrical lead, *5*) mixing device with break seal.

The most critical elements of fluorine bomb calorimeters are the seals and the locking devices. Hubbard and coworkers used simple gold[9] and aluminium[10] gaskets, or gold–Teflon gaskets[8], to seal the lids of their single-chamber bombs; Armstrong and coworkers[67] used Teflon seals. A single-chamber calorimetric bomb of 350 cm^3 capacity[32,33], made of Monel metal, is shown in Fig. 3. It relies on aluminium seals with Teflon-filled channels. We have also used Teflon seals designed on the self-tightening principle[78,79]. Various other effective sealing arrangements for fluorine bomb calorimeters have been described[78-81].

¶The calorimetric bombs are designed to be used in conjunction with the most widely used type of calorimetric system: the water calorimeter with an isothermal enclosure.

†We shall not attempt to describe the glass apparatus for fluorine calorimetry used by Gross and coworkers[2,13,15,35,36,41] because of its limited pressure range, difficult operating procedure, and liability to attack on the glass. Some other unusual approaches[17,63] will also be ignored.

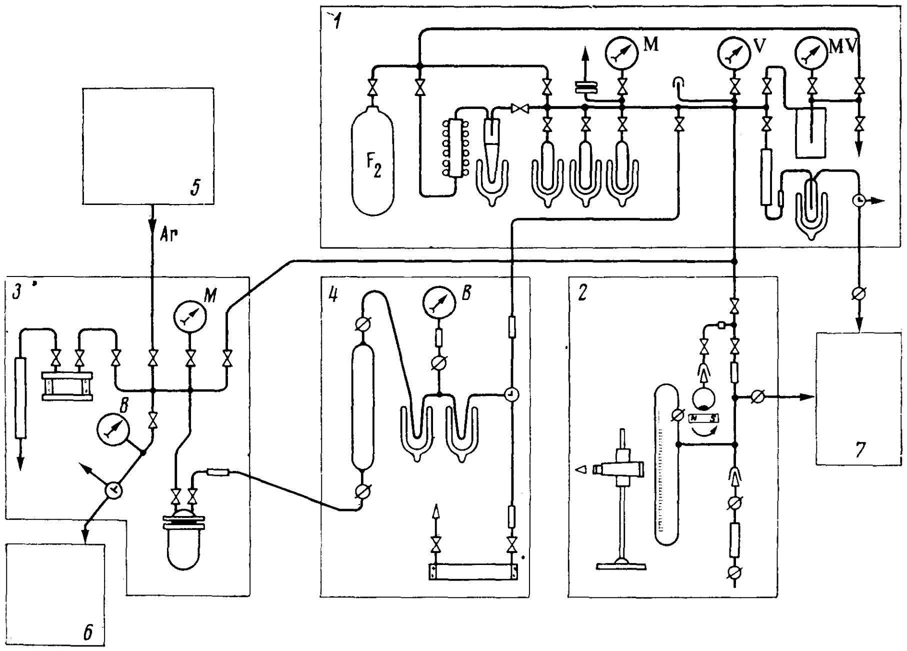

Figure 5. Fluorine handling apparatus for calorimetric work: *1*) purification and storage train, *2*) fluorine analysis, *3*) bomb filling assembly, *4*) assembly for collecting and separating the gaseous combustion products, *5*) argon purification, *6*) and *7*) backing pump and vacuum pump, M) manometer, V) vacuum gauge, MV) combined manometer and vacuum gauge.

As stated above, the possibility of spontaneous reaction can be a serious problem in calorimetric work with fluorine in a bomb. It may be necessary to prevent contact between the reactants until the beginning of the main period of the calorimetric experiment. The commonest solution of this problem is to use a two-chamber bomb. A widely used type of two-chamber bomb was designed by Hubbard and coworkers[82,83]; our own design (Fig. 4) is described in Ref. 79. The two-chamber bomb described by Barberi and coworkers[63] was not so successful. Alternative means of isolating the sample from the fluorine in a single-chamber bomb have also been proposed. Thus, Schröder and Sieben[6] measured the heats of combustion of tungsten pentafluoride and of elemental sulphur, which ignite spontaneously in fluorine, in a single-chamber bomb fitted with a nickel vessel and external means for opening and shutting the lid of this vessel. The weighed sample was placed in the nickel vessel, which remained filled with argon until the beginning of the main period. A similar device was used by Bisbee and coworkers[61,64] to measure the heat of the reaction between ClF_5 and hydrogen. A thin-walled Monel metal bulb, previously filled with ClF_5, was placed in the bomb and punctured with a special device, thus allowing the ClF_5 to react with the hydrogen filling of the main chamber.

Other methods, described in the following Section, use an auxiliary material (which does not react spontaneously with fluorine) to isolate the sample from the fluorine in a single-chamber bomb. The partition is ignited when contact between the sample and the fluorine is required.

Fig. 5 shows a typical assembly for handling fluorine in calorimetric work. It is more complicated than some other designs[3,68] because it includes all the necessary subsidiary facilities such as apparatus for purifying and storing the fluorine (*1*), for analysing the fluorine by the mercury method (*2*) including provisions for sampling the residual gases, for filling the bomb (*3*), and for sampling and separating the gaseous combustion products including provisions for duplicate analysis of the excess fluorine and for sampling gaseous fluorides (*4*). Facilities for purifying the argon used to purge the apparatus (*5*), and for producing a rough vacuum (*6*) and a high vacuum (*7*), are also shown. Items *1* and *3* are made of nickel, with stainless steel valves and taps. Items *2* and *4* are made of quartz and Pyrex glass. The glass vacuum joints are lubricated with a special perfluorinated grease.

We have already pointed out that corrosion of the apparatus and (particularly of the bomb) in fluorine can lead to major difficulties in high-precision measurements. The following precautions are taken to ensure that the results are not affected by side reaction of the construction materials with the fluorine or with the fluorides produced by the combustion. First, all the metal vessels and connecting tubes are tested under pressure, under vacuum, and they are then exposed for several days to fluorine at its working pressure‡. Furthermore, a number of "blank" combustions of the sample are carried out in the calorimetric bomb[31-34]. The products of these combustions are tested for the presence of products of any reactions between the fluorine and the bomb materials, the sample supports, and the passivating fluoride films which are formed on

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‡Wise and coworkers[11] describe a method of passivating the calorimetric apparatus by heating it for several hours at 110° in the presence of fluorine at 1 atm pressure.

their surface[32,34]. The success of the passivating treatment is checked by separately weighing the internal components of the bomb[32].

Secondly, all operations (loading and unloading) with the passivated bomb are carried out in a "dry" box§ to avoid the danger of hydrolysis of the passivating fluoride film. The other parts of the apparatus are kept filled with dry argon after passivation[32]. Additional tests include check measurements of the water equivalent of the calorimetric system by calibration[85] before and after each series of experiments. Electrical calibration is preferred, but the combustion in oxygen of calorimetric standards such as benzoic acid is also acceptable[3,32,33].

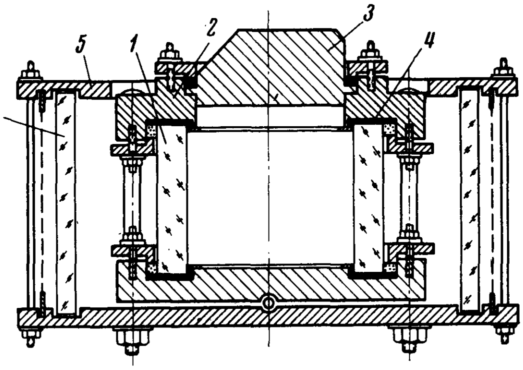

Figure 6. Glass bomb for experiments on the optimum conditions for fluorine combustion: *1*) glass body, *2* nickel flange, *3*) lid, *4*) seal, *5*) explosion guard.

A glass bomb for test combustions in fluorine is a valuable facility for auxiliary experiments aimed at selecting the best combustion conditions for the calorimetric bomb. The bomb (Fig. 6) has transparent walls through which the reactions in the chamber can be visually observed at fluorine pressures up to 10 atm. The apparatus was first used by Hubbard and coworkers[84]; our modification, shown in Fig. 6, was described in Ref. 78.

Special safety precautions are essential in all laboratory work involving liquid fluorine and gaseous fluorine under pressure. The danger of explosions and the high toxicity of fluorine and fluorides must be carefully considered in the design of the apparatus, the layout of the accommodation, and the choice of operating procedure[3,68,71,74,85].

V. COMBUSTION METHODS

The main consideration in the search for the optimum combustion conditions is the nature of the reaction between the sample and the fluorine. The geometry of the sample (assuming, of course that the sample is not gaseous) is of crucial importance. Hubbard[3] has made a special study of this problem, and has even suggested a classification of combustion methods based on sample geometry¶.

It can be seen from the Table that metals account for a significant proportion of the materials which have been investigated by this method. When metallic samples are burned in fluorine under bomb conditions the temperature can be high enough to melt the sample, at least partially. The effect depends markedly on the rate of reaction of the metal with fluorine. If the rate is high, and the resulting fluoride has a low boiling point (e.g. tungsten[6,31-33]), there is little danger of side reactions leading to analytical complications. On the other hand if the rate is relatively low, the thermal conductivity of the sample is high, and the resulting fluoride is involatile, the molten metal tends to break up into drops and to spatter, together with some of the fluoride formed by the reaction. This effect can have various undesirable consequences, particularly at the contact between the metal and the support. It can be avoided by diluting the fluoride with an inert gas so as to lower the temperature and the reaction rate.

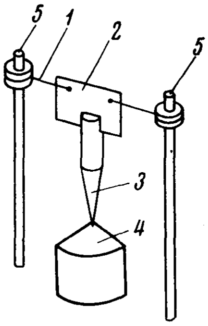

Figure 7. Combustion of metallic zirconium in fluorine: *1*) zirconium igniting wire, *2*) zirconium foil, *3*) pointed zirconium rod, *4*) massive nickel block.

Thus, in the first investigation by fluorine bomb calorimetry described by Hubbard and coworkers[8] the sample of zirconium metal (of the shape shown in Fig. 7) was burned from the top towards the bottom. The reaction stopped after ~75% of the sample had been burned, owing to the loss of heat to the massive nickel heat sink. Fusion of the zirconium was avoided by diluting the fluorine with helium (fluorine pressure 2000 mmHg, total pressure 12 atm). A similar method was used by Hubbard and coworkers in their calorimetric work with metallic uranium[16].

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§However, it has been pointed out[11,37] that the water equivalent of the calorimetric system is practically unaffected by storing the passivated nickel bomb in ordinary air and by washing it in water.

¶There are, of course, other classifications, e.g. classifications according to the phase composition of the products (gaseous, fused, or solid), or according to the number of products (only the higher fluoride if the reactant is an element or a lower fluoride, but if the sample is more complex several products may be formed, and may have to be separated for analysis). Alternative methods of classification could be based on the use of auxiliary materials, on the ignition procedure, on the propensity to spontaneous reaction with fluorine, etc.

When metallic copper[33], zinc[21], cadmium[19], magnesium[22], or nickel[37] are burned in fluorine an acceptable rate of combustion is obtained only at temperatures in excess of the melting point of the metal. Several workers[19,21,22,24,26,37] have therefore been compelled to line the inner surface of the bomb and to use a substrate made from a fused fluoride of the metal under test. It was assumed that under these conditions no undesirable reactions can occur between the metal and the substrate in a fluorine atmosphere. However, oxygen evolution was observed in the bomb during the combustion of metallic nickel[37] in the presence of high pressures of fluorine (15–25 atm). Evidently the NiF_2 substrate still contained some nickel oxide in spite of having been carefully prepared by lengthy baking in HF and ClF_3. Side reactions with formation of copper monofluoride between molten copper and the CuF_2 substrate could not always be avoided in calorimetric combustions of metallic copper[33,86].

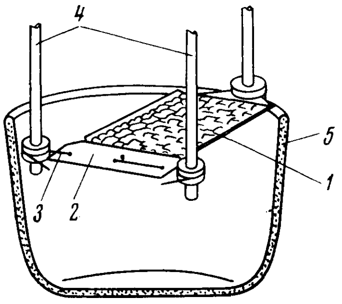

Figure 8. Combustion in fluorine of a copper sample with tungsten: *1*) copper sample (gauze), *2*) tungsten sheet, *3*) tungsten igniting wire, *4*) electrodes, *5*) fused alumina heat screen.

The possibility of forming lower fluorides and the difficulty of separating and analysing the combustion products can preclude the use of "inert" fluoride substrates. In these circumstances it is better to use an auxiliary material whose combustion can raise the temperature in the reaction zone. In this way the rate of the main reaction is increased, and the resulting fluorides are volatilised and condense on the cold walls of the bomb. Drop formation and spattering of the molten metal can be avoided by keeping the rate of fluorination high and the thermal conductivity of the sample low. Analysis and identification of the combustion products becomes much simpler if the conditions are chosen so that only gaseous products are formed in the combustion zone. Another important consideration is the possibility of working at much lower initial pressures of fluorine if an auxiliary material is introduced as an igniter.

We have used this procedure to measure the enthalpy of formation of CuF_2 by burning metallic copper in fluorine[33], and also in seeking the best conditions for the combustion of metallic nickel in fluorine. The type of copper sample[33] is illustrated in Fig. 8. The auxiliary material was metallic tungsten. The geometry of the sample ensures the maximum concentration of heat at the combustion front. Domalski and Armstrong used a similar method in their calorimetric combustions in fluorine of metallic aluminium[23], one of the boron carbides[52], and aluminium boride[48]. Their samples consisted of pressed disks of the powdered material (aluminium, aluminium borides, or boron carbide) mixed with powdered Teflon which they found to be a suitable igniter for these reactions[23,48,52].

Ill-defined reaction products, including lower fluorides, are occasionally obtained when some metals are burned in fluorine. As was pointed out above, this difficulty was encountered in our work on the combustion of copper[33]. In the determination of $\Delta H_f^\circ(UF_6, g)$ by the combustion of metallic uranium in fluoride[16] small amounts ($\sim$1%) of lower uranium fluorides were invariably produced in the bomb, requiring very accurate chemical analyses to enable the appropriate corrections to be calculated. Careful analyses of the solid "residues" of lower fluorides had to be made also in other investigations[10,29].

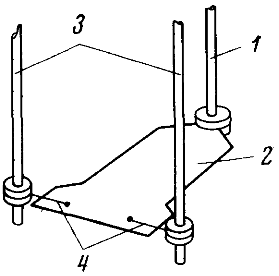

Figure 9. Combustion of a metallic tungsten sample in a fluorine bomb: *1*) holder, *2*) tungsten foil, *3*) electrodes, *4*) tungsten igniter wire.

In spite of these difficulties, it is often possible to choose a type of metal sample for combustion (foil, wire, or rod) which avoids or minimises the substrate problem. The geometry of the sample and the method of clamping the sample in the bomb are usually determined by the need to avoid direct contact between the combustion zone and the constructional materials (substrate, bomb fixtures). The design of tungsten foil sample shown in Fig. 9, used for calorimetric combustions at fluorine pressures up to 3 atm[32], satisfies all these requirements. The tungsten foil, 0.06 mm thick, can be burned completely without undesirable effects such as spattering or contamination of the combustion zone by falling fragments of the sample support.

When powdered samples are used for calorimetric combustion in a fluorine bomb they are usually contained in a simple nickel capsule or crucible. Contact between hot particles and the container material leads to local overheating and enhanced corrosion of the nickel. Various practical steps can be taken to minimise this effect. The burning rate of the particles can be decreased by diluting the fluorine with helium or argon, and by choosing the most appropriate particle size for the sample[11]. Alternatively, massive containers can be used to conduct the heat away from the reaction zone[50]. Occasionally it is possible to use a container material which avoids the danger of side reactions between the combustion products of the main sample and the passivating fluoride film of the constructional material. For example, Hubbard and coworkers[50] used a container of metallic zirconium in their study of zirconium diboride. Often the container material is chosen empirically. Containers of fused alumina or nickel had been found[11] to react with fluorine at the points of contact with a charge of crystalline boron powder. They were successfully replaced by a CaF_2 crucible. Combustible containers, which fulfil the role of igniter, have also been used[33,48,52].

A test for the absence of "premature" reaction between the sample and the fluorine is an essential part of the search for the optimum combustion conditions (unless of course the design of the bomb allows physical isolation of the two reactants). The test usually takes the form of repeated weighings of the sample after exposure to fluorine in the bomb at the working pressure. If the premature reaction is significant the simple test is followed by analytical determinations. Hubbard and coworkers burned metallic uranium[16], and niobium and tantalum[25], in a single-chamber bomb after determining the extent of the preliminary reaction with fluorine. They showed that this reaction (between uranium and fluorine) produces uranium tetrafluoride[16], and they were able to correct their calorimetric measurements accordingly.

We have already pointed out that the most effective and generally applicable precaution in the study of materials which ignite spontaneously in fluorine is to use a two-chamber bomb. The other methods of isolating the reactants mentioned in the previous Section are attempts at designing a "universal" bomb[6,64]. It is appropriate at this point to review the methods of isolating the reactants by using auxiliary materials as combustible partitions in one-chamber bombs. Thus, Margrave and coworkers[43,55] used a nickel vessel with a pressure-tight lid including a tungsten foil diaphragm. The vessel, containing a weighed amount of the sample, was filled with helium and inserted into the calorimetric bomb, which was filled with fluorine. At the beginning of the main period of the calorimetric experiment the foil was kindled with an igniter wire, thus allowing the fluorine to reach the sample. The review articles by Hubbard[3] and Armstrong[68] suggest the use of quartz bulbs[3] sealed by a small stopper of thin Teflon[68] or metal foil[3].

A number of conditions must be satisfied when auxiliary materials are used in calorimetric combustions in fluorine. The main condition is an appropriate choice of the auxiliary material itself. As well as being compatible with the chosen method of combustion, it must have an accurately known heat of combustion in fluorine. Also, its fluorination products should be inert towards the fluorination products of the main sample. The presence of an auxiliary material introduces additional measurement difficulties. In order to obtain accurate results the heat of combustion in fluorine of the auxiliary material must be determined in a separate series of experiments, using the same sample geometry and identical bomb conditions (initial fluorine pressure, amount of material, method of supporting the sample). These precautions ensure that the result is unaffected by impurities and by uncontrolled combustion conditions[23,33].

Preliminary measurements of the heat of combustion in fluorine of the auxiliary material were made in all the thermodynamic investigations listed in the Table which relied on an auxiliary material. Thus, Hubbard and coworkers measured the heat of combustion of sulphur in fluorine[5], and subsequently used this material to initiate the combustion of molybdenum and vanadium sulphides[44,56] and of niobium and tantalum borides[51] in a two-chamber bomb. Precise measurements of the heat of combustion of silicon in fluorine[18] enabled Hubbard and coworkers to use silicon as an initiator for graphite[39] and silica[18]. Armstrong and coworkers repeatedly measured the heat of combustion of Teflon in fluorine[23,38], and they used Teflon as the auxiliary material in their studies of the heat of combustion of aluminium, graphite, aluminium borides, etc.[23,38,48] Tests for possible interactions between the fluoride of the main sample and that of the auxiliary material are made by various methods, described below.

Other workers have used tungsten[33,43,55], sulphur[44,51,56,58], silicon[18,39], Teflon[23,38,48,55], phosphorus trifluoride[59], titanium[11], and molybdenum[12] as the auxiliary material. Tungsten, titanium, and molybdenum in the form of thin wires can be used to ignite samples by the electrical discharge method[11,12,33,43].

It is evident from the above discussion that the combustion of samples in fluorine in a calorimetric bomb can be carried out by very different procedures. The most important criterion for choosing the best combustion conditions is freedom from side reactions. Equally important is the provision of simple, reliable, and accurate methods of analysis of the bomb products.

It may be useful to dwell in some detail on some differences in the analytical techniques used to identify the products of combustion in fluorine. These differences arise mainly from the need to estimate the excess of fluorine and the gaseous products of the combustion in fluorine, as well as identifying any interactions with the bomb materials.

Analysis of the excess of fluorine involves the separation of the gaseous fluorides by low-temperature vacuum condensation. It has been shown[18,41,47,60,66] that the combustion of many oxides in a fluorine bomb produces the corresponding fluoride and oxygen; nitrogen is formed when nitrides[49,57] and some other nitrogenous compounds are burned (e.g. thiazyl trifluoride[59]). Most of the other elements burn with formation of higher fluorides. Thus the excess of fluorine may contain amounts of oxygen, nitrogen, and some fluorides (CF_4, BF_3, SF_6, etc.) corresponding to the stoichiometry of the reactions under study. Because the boiling points of these materials are not very different from that of fluorine we cannot expect complete separation by the low-temperature vacuum condensation method. The excess of fluorine may contain also additional amounts of oxygen, nitrogen, carbon tetrafluoride, etc. produced by the combustion in fluorine of impurities in the main sample. Hence a study of the composition of the residual gas after absorption of the fluorine in mercury is an essential analytical operation. For example, King and Armstrong[66] showed, by chromatographic separation of the components of the gaseous residue, that free oxygen is formed by the reaction between oxygen difluoride and hydrogen. I.r. and gas-chromatographic analyses of the residual gases enabled O'Hara and Hubbard to show[34] that phosphorus pentafluoride is the only product of the reaction between phosphorus and fluorine under calorimetric bomb conditions. Hubbard and coworkers[49] proved, by mass-spectrometric analysis of the gaseous residue, that free nitrogen and boron trifluoride are formed in the reaction between boron nitride and fluorine.

If the reaction under study gives rise to a mixture of volatile fluorides, which is invariably the case when auxiliary materials are used, the possibility of side reactions between the fluorides must be examined. This problem can also be solved by the analytical procedures described above. Special experiments are sometimes needed. Thus, the absence of interactions between boron trifluoride and tungsten hexafluoride during the combustion of tungsten borides in fluorine[58] was demonstrated by volumetric experiments with mixtures of these gases. Gross and coworkers[36] tested for interactions between phosphorus pentafluoride and boron trifluoride, in their work on the heat of formation of boron phosphide, by a series of calorimetric experiments in which equimolar mixtures of boron and phosphorus (and separate samples of boron and phosphorus) were burned in fluorine.

Gas chromatography is perhaps the most convenient method of analysis of the gaseous products of combustion in a calorimetric fluorine bomb (including the excess of fluorine)†.

The solid products of the reaction between the sample and fluorine can be analysed by chemical and X-ray diffraction methods[33,37]. Solid reaction products are separated from the unburned part of the sample by appropriate choice of combustion conditions. The extent of side reactions with the sample support materials is checked at the same time. If necessary, the results of these analyses are used to calculate corrections to be applied to the calorimetric measurement. The correction for attack on a nickel support has been specially discussed[34,58].

VI. CONCLUSIONS

The above discussion of the special features of reaction calorimetry in a fluorine bomb gives some insight into the aspects which must be considered before deciding to use this method in specific instances. The method is relatively complex and laborious, since it requires special experimental procedures and a large number of analytical checks. We have tried to make clear the extent to which thermochemically well defined conditions can be achieved in fluorine bomb calorimetry.

After applying the corrections for side reactions the calorimetric result is calculated by normal procedures[74]. However, there are some differences of detail in the calculation of the correction for standard conditions. Thus the determination of the Washburn corrections (for the change in internal energy of the system when converted to the standard conditions) can present some difficulty due to the lack of necessary data. A method of calculating the Washburn correction from the coefficient $(\partial E/\partial p)_g$ for fluorine and gas mixtures containing fluorine, measured in a separate experiment by Hirschfelder's method, has been described by Hubbard in detail[3]. Calculations of the correction for reactions with impurities in the sample usually assume that oxygen and nitrogen are evolved in the free state during combustion in fluorine. All other impurities are assumed to form higher fluorides[32,33,57].

When a double-chamber calorimetric bomb is used, the heat associated with the transfer of the fluorine into the combustion chamber has to be measured by a series of "blank" calorimetric experiments with a bomb containing the fluorine but not the main sample. The results are used to apply a correction to the calorimetric results of the main experiment[5,7,44,46].

One fundamental problem in the adoption of fluorine bomb calorimetry is the lack of a really satisfactory standard material. Calibration standards for combustion in fluorine should meet the following requirements[3]: their heat of combustion in fluorine should be reliably and accurately known, the combustion and analysis procedures should be simple and the reaction should be thermochemically well defined, there should be no side reactions with fluorine or with impurities in the fluorine, and lastly the material should be available in a high state of purity. We believe[33] that metallic tungsten satisfies all these requirements. The value $\Delta H^\circ_{f\,298\cdot15}(WF_6, g) = 411.4 \pm 0.2$ kcal mole^{-1} appears to be well established[32,33]. It agrees well with the results obtained in two other laboratories[6,31]. The procedure for burning tungsten in fluorine[32,33] is relatively simple (see Fig. 9): the only combustion product is gaseous tungsten hexafluoride, which can easily be separated from the excess of fluorine for subsequent analysis by vacuum condensation[31-33].

Standardisation of some of the auxiliary procedures (in particular, the fluorine analysis) would be desirable. Our procedure and apparatus[75], described in Section III, give accurate analytical results after a relatively simple purification of the fluorine, and can be recommended as the preferred method of fluorine analysis in calorimetric work. Our method of passivating the calorimetric bomb, and the operating conditions, can also be recommended. We also believe that the initial pressure of fluorine in the bomb should be as low as possible. We have shown that the maximum pressure of fluorine can be limited to 8–10 kg cm^{-2} even with samples of metallic copper and nickel, which can be classified as "difficult" because of their inertness towards fluorine. The tendency to use lower fluorine pressures is justified by the lower corrosion rate of the bomb materials in low-pressure fluorine.

This brief review suggests that the experimental problems encountered in the use of a fluorine bomb in reaction calorimetry have been solved to a large extent. More accurate and better standardised experimental approaches are needed to extend the range of applications of the method, which is still considered to be a laborious and specialised procedure, and to allow its advantages to be fully realised. It is clear from the results listed in the Table that although the stage of determining the heats of formation of simple fluorides is far from complete, there are already indications that the method can be applied to complex materials. Examples of the successful application of fluorine calorimetry in the study of compounds include the fluorine combustion of SiO_2, B_2O_3, and GeO_2, which provided the first reliable values of the enthalpy of formation of these compounds. The reaction with fluorine is the most convenient method of measuring $\Delta H^\circ_{f\,298}$ of several refractory compounds, especially borides and silicides, as well as the lower fluorides. We can expect the range of applications of fluorine calorimetry to continue to expand, and in future the method is likely to become one of the most widely used thermochemical procedures.

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†A gas chromatograph for the analysis of aggressive and easily hydrolysable materials (KhG2302) has recently been developed by the Analytical Instrumentation Division of the USSR Academy of Sciences. This apparatus can be used for the analysis of gas mixtures containing fluorine.

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The Interaction of Organometallic Derivatives with Organic Halides

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The possible mechanisms of the reactions of organometallic derivatives with organic halides, including the metal-halogen and recombination (Wurtz) reactions, are examined. Particular attention is devoted to the analysis of the composition of the products and the stereochemistry of the reactions and to the results obtained using physicochemical methods. The bibliography includes 156 references.

CONTENTS

I. INTRODUCTION

The interaction of organometallic compounds RM with alkyl halides R′X is a complex process which may proceed as an exchange reaction (known for sodium, lithium, magnesium, and barium derivatives):

$$RM + R'X \rightarrow RX + R'M,$$

or as a recombination reaction (the well known Wurtz reaction involving RLi or RNa):

$$RM + R'X \rightarrow R{-}R',$$

accompanied by the formation of RR, R′R′, RH, R′H, R(−H), and R′(−H). The problem of its mechanism is still controversial and the possibility of heterolytic and radical pathways is being discussed.

A tendency has arisen in recent years to consider many reactions previously classified as nucleophilic or electrophilic substitution processes in terms of oxidation–reduction interactions. Within the framework of this concept, the interaction of a donor (nucleophile) and acceptor (electrophile) takes place as a result of electron transfer (*single electron transfer*, SET mechanism) and leads to the formation of radicals or radical-ions. There is no doubt that the objective cause of the development of this concept (and the reason why it has proved attractive) has been the appearance of physicochemical methods whereby one can detect the formation of radical-ion and radical species directly or indirectly the latter method includes chemically induced dynamic nuclear polarisation (CIDNP).

Naturally the attention of the supporters of this concept has been attracted primarily by organometallic compounds which can behave, by virtue of their high capacity for oxidation, as electron donors in relation to many organic and inorganic acceptors. The first attempts to consider certain reactions of organometallic derivatives with carbonyl compounds and alkyl halides from the standpoint of a radical mechanism were made as early as the beginning of this century on the basis of the composition of the observed products or the appearance of a colour in the reaction mixture, although the formation of "anomalous" products in many instances could be accounted for also within the framework of a heterolytic mechanism. However, the possibility of the simultaneous occurrence of reactions via several pathways was hardly ever considered, although the question of the possible change from an ionic to a radical mechanism frequently arose when the nature of the metal atom, the structure of the reactants, and the reaction conditions (primarily temperature and the solvent) were altered.

Attempts are now being made to unify the two mechanisms within the framework of the concept of single electron transfer (SET), as a result of which there is radical recombination with formation of RR′ (the classical Wurtz reaction) and the formation of products arising from the radicals R· and R′· liberated from the cage can occur.

From the standpoint of the SET mechanism, the general scheme for reactions of RM with R′X can be represented as follows:

$$RM + R'X \rightleftarrows \begin{bmatrix} R'^{\cdot} & X^{-} \\ R^{\cdot} & M^{+} \end{bmatrix} \longrightarrow \begin{cases} \xrightarrow{\;a\;} R{-}R' \\ \xrightarrow{\;b\;} R'M + RX \\ \xrightarrow{\;c\;} R'^{\cdot} + R^{\cdot} \end{cases} .$$

In this review we attempted to analyse all the mechanisms of both exchange and Wurtz reactions which are being discussed in the literature, without trying to cover the entire available data and all the synthetic aspects of these reactions. It was found that the simple SET mechanism cannot explain all the observed characteristics of the reaction between R′X and RM. This applies particularly to stereochemical data, since reactions of organometallic compounds with optically active halides, which lead not only to racemisation but also to inversion (in the Wurtz sense) and to racemisation with partial or complete retention of configuration (in the metal-halogen exchange reactions), are known.

II. REACTIONS WITH ORGANOMAGNESIUM COMPOUNDS

The first systematic study of the reactions of organomagnesium compounds with alkyl halides was apparently undertaken in 1913 by Späth[1], who proposed a radical mechanism, in contrast to Abegg's ionic mechanism[2]. In many cases the main reaction products were the hydrocarbons R_2, R'_2, R(–H), RH, etc., which had been previously regarded as side products, and not the mixed hydrocarbon RR′ (the product of the Wurtz reaction). It is interesting to note that the hydrocarbon RR′ was formed in a high yield when halogeno-derivatives of the allyl and benzyl types or derivatives with a tertiary group R were introduced into the reaction[1–4]. As will be shown below, the same effect is observed also in the corresponding reactions of organosodium and organolithium derivatives with yields of the hydrocarbon RR′ reaching 70–98%.[5–9] It is difficult to account for these results from the standpoint of a radical mechanism, since the extent of the liberation of the radicals from the cage should increase with increase of their stability. Indeed, when R = Ph_3C, a large amount of triphenylmethyl radicals of triphenylmethyl peroxide is always formed in the reaction[10–14]. For example, the yield of tetraphenylmethane in the reaction of Ph_3CCl with PhMgBr has been usually 0.5–5%[10] and the yield increased to 12% only under specially selected conditions (temperature, solvent, order of addition of reactants)†. The replacement of phenylmagnesium bromide by the corresponding iodide led to the formation of the triphenylmethyl radical and biphenyl alone (not even traces of Ph_4C were detected).[11] The yield of tetraphenylmethane in the reaction of PhMgBr with triphenylmethyl ethers Ph_3COR (R = Me, Et, or Ph) reached 10–12% for the first two groups and was more than 20% in the reaction with phenyl ether at 150°C. The last reaction occurred most readily, but the reduction of temperatures to about 35°C led to the formation of triphenylmethyl peroxide alone[10]. However, one should note that exceptionally high yields of Wurtz reaction products are formed even with triphenylmethyl halides when benzyl (or methyl) Grignard reagents are introduced into the reaction[1,2,15,16].

In certain early studies, the formation of R'_2 alone was observed when RMgX was allowed to react with R′X. Thus according to Schmidlin and Massini[17], the only product found in the reaction of phenylmagnesium bromide with β-chloromethylnaphthalene was symmetrical di-(β-naphthyl)ethane. A similar result was obtained by Fuson[18], who isolated the corresponding bibenzyl $(o\text{-}CNC_6H_4CH_2)_2$ after the reaction of methylmagnesium bromide with o-cyanobenzyl bromide. On this basis, he suggested that the Grignard reagent promotes the radical reaction of R′X.

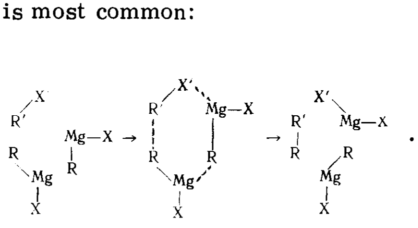
All the early studies suffered from one disadvantage—the lack of a complete analysis of the products and in the first place from the loss of volatile hydrocarbons. The first disadvantage was apparently overcome by Fuson[19], who analysed in detail the products of the reaction of MeMgI with benzyl halides (Hal = Cl, Br, or I) and showed that, apart from ethylbenzene and bibenzyl, which had been detected also by other investigators[1,4], ethane is formed in the reactions in equimolecular amounts with respect to bibenzyl. We may note that the yield of ethylbenzene decreased appreciably in the sequence $PhCH_2Cl > PhCH_2Br > PhCH_2I$ (by a factor of about 2.5 on passing from the chloride to the iodide); the amounts of ethane and bibenzyl increased under these conditions, albeit only slightly (to an extent of about 20%). These results can be accounted for from the standpoint of both the SET mechanism, i.e. by a change in the ease of rupture of the C–Hal bond in the above sequence and by the occurrence of two consecutive reactions—exchange and Wurtz reactions, since the possibility of the exchange processes also increases on passing from the chloride to the iodide. However, the author himself believed that the exchange reaction has no bearing on the formation of ethane, since he had shown for benzyl chloride that methyl chloride is absent from the reaction products:

$$PhCH_2Cl + CH_3MgI \rightarrow CH_3Cl + PhCH_2MgI,$$

and furthermore in the reaction of methyl iodide with CH_3MgI ethane is formed in a yield of only 21%:

$$CH_3I + CH_3MgI \rightarrow CH_3CH_3.$$

The possibility of a radical mechanism was considered by Gilman and Kirby[20], who observed that the reaction of diphenylmethylmagnesium bromide with dimethyl sulphate leads to the almost quantitative formation of tetraphenylethane. However, in their book dealing with organomagnesium compounds[21], Kharash and Reinmuth noted the possibility of a radical mechanism of the Wurtz reaction and expressed the view that this pathway probably occurs only rarely on the grounds that there is no statistical distribution of hydrocarbons in the reaction products (RR′, R_2, and R'_2) or the corresponding disproportionation products [RH, R(–H), R′H, and R′(–H)]. We may note that, from the standpoint of the SET mechanism, this argument appears unconvincing, since the ratio of the yield of recombination products and the extent of the liberation of radicals from the cage can vary within wide limits, depending on the stability of the radicals and the reaction conditions. As a second argument, Kharash and Reinmuth quote the fact that in real radical processes, which were believed to be the reactions of R′X and RMgX in the presence of transition metal salts, quite different products are formed. Finally, the main argument was the fairly high yields of the hydrocarbons RR′ observed for R = $PhCH_2$, $CH_2=CH-CH_2$, CH_3OCH_2, etc., i.e. in those reactions where fairly stable radicals should have been formed‡. Kharash suggested that there is no unique mechanism explaining all the observed instances of the reactions; he believed that the trimolecular "push-pull" mechanism is most common:



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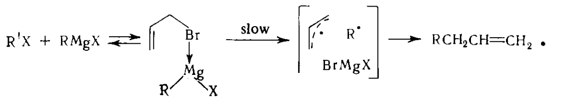
† Gilman and Jones[15] observed the formation of 47.7% of p-biphenylyldiphenylmethane (not detected by other workers), which undoubtedly confirms the presence of Ph· in the system.

‡ We may note that the absence of a β-hydrogen atom is a characteristic feature of all the groups enumerated as well as CH_3.

The view that, depending on the structure of the reactants and the conditions in the reaction, the mechanism of the latter may change, was questioned by Gough and Dixon[22], who investigated the kinetics of the reaction of allyl bromide with a series of organomagnesium compounds. In terms of their reactivity, the derivatives RMgX were arranged in the following sequence:

RMgX	PhMgBr	n-BuMgCl	s-BuMgCl	t-BuMgCl
$K_{\text{rel, 25°}}$	1	2.71	22.6	107

According to the authors, the observed sequence in which the reactivity varies and the applicability of the Taft equation with $\rho = -1.9$, the formation of 2,2,3,3-tetramethylbutane in the reaction with t-BuMgCl, and the ESR signal observed in the reaction with n-BuMgCl (although the yield of n-BuCH$_2$–CH=CH$_2$ was 90%) indicate the SET mechanism:



The conclusion that the reaction of phenylmagnesium iodide with iodobenzene has a radical mechanism was based on the detection of the label in the reaction product when deuterobenzene was used as a solvent (in admixture with ether).[23]

The composition of the products formed in the reactions of phenylmagnesium bromide and benzylmagnesium bromide with a series of arylalkyl chlorides is regarded[24] as proof of the SET mechanism, since, according to Gilman's data[15], exchange processes do not occur in these systems.

R'X	RMgX	Yield, % RR'	R'R'	RR	RH
PhCH$_2$Cl	PhMgBr	56	6	4	12
(Ph)$_2$CHCl	»	60	6	6	10
Ph$_3$CCl	»	46	5	4	10
Ph$_3$CCl	PhCH$_2$MgCl	55	5	15	—

The observed reactivity series Ph$_3$CCl > Ph$_2$CHCl > PhCH$_2$Cl, PhCH$_2$MgX > PhMgX, which is the same as the series based on the increasing stability of the groups R and R', is also consistent with the radical reaction mechanism. A similar mechanism has also been proposed[156] for the reaction of phenylmagnesium bromide with bromotriphenylmethane on the basis of the analysis of the composition of the products. When the reaction was carried out in ethyl ether, triphenylmethanol, triphenylmethane, biphenyl, ethylbenzene, and α-phenylethyl alcohol were detected in the reaction mixture, while in the presence of oxygen triphenylmethyl peroxide was found.

Finally, data confirming that alkyl radicals are formed even in the reactions of alkylmagnesium halides with "simple" alkyl halides have been obtained in recent years. This is indicated by data based on the CIDNP of the reaction products. Thus Ward et al.[25] observed CIDNP in the products of the reaction of t-butyl bromide with t-butylmagnesium chloride and of n-butyl iodide with n-butylmagnesium chloride in tetrahydrofuran (THF). The former reaction leads to the formation of isobutene (6%), isobutane (39%), and tetramethylbutane (6%), the vinyl protons of isobutene and but-1-ene and the methyl protons of isobutane being polarised, which suggests the formation of t-butyl and n-butyl radicals§.

CIDNP was likewise observed in the products of the reaction of diethylmagnesium with ethyl iodide and isopropyl iodide in THF.[26] The disproportionation products of the groups R and R' were mainly formed (ethane, ethylene, propane, and propene) with only a small amount of recombination products. The initial iodides were also polarised, which is associated, according to the authors, with a relay transfer of the radical in the chain process:

$$R'I + R^{\cdot} \rightarrow R'^{\cdot} + RI.$$

The authors believe that exchange processes can be hardly responsible for the observed polarisation of the halide, since in the reactions of iso-PrI with Et$_2$Mg the exchange process would have led to the formation of appreciable amounts of ethyl iodide, which was not observed under the conditions of the NMR experiment. However, the reaction of diethylmagnesium with iodobenzene occurred mainly as an exchange process:

$$\underset{}{Et_2Mg} + PhI \rightarrow \underset{72\%}{Ph_2Mg} + \underset{92\%}{EtI} + \underset{5\%}{PhH} + \underset{5\%}{PhEt},$$

The yield of ethylbenzene increased with time owing to the condensation of Ph$_2$Mg with EtI.

Ideas concerning the mechanism, including SET, of reactions involving ArHal (the Wurtz–Fittig reaction) have been put forward[27] on the basis of the detection by ESR of radical-anions in the reaction of phenylmagnesium bromide and phenyl-lithium with nitrosated halogenobenzenes.

When the results of the reactions are considered from the standpoint of the SET mechanism, then evidently the ratio of the radical recombination products and products arising as a result of the liberation of radicals from the cage should depend on the structure of the radical and also on the stabilities of the individual components of the radical-ion pair. For example, the reaction of 1-adamantyl bromide with a series of organomagnesium compounds RMgX can be analysed from this standpoint[28]. For R = Me, the Wurtz reaction was achieved with an 83% yield, but the latter fell sharply for R = PhCH$_2$ and became zero for R = t-Bu, where adamantane was formed in 84% yield. However, there exists an alternative explanation, which Osawa et al. in fact believe to be valid[28], namely that the reaction mechanism changes when the group R in RMgX alters.

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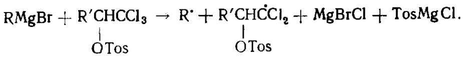
§ The recently published study by Ward and coworkers[155] suggests that even a small admixture of transition metals present in magnesium can alter significantly the nature of the reaction of RMgX with R'X and can stimulate the development of a radical reaction pathway. The authors showed that the rate of reaction of iso-PrMgBr with iso-PrBr, leading to propane and propene, increases sharply following the addition of bromine, the effect being more marked when less pure magnesium (99.9 instead of 99.998%) is used; a considerable polarisation of the reaction products was observed at the same time. It is suggested that the process is catalysed by an oxidised form of the metal, for example the metal oxidised by the halogen present in R'X. We may note that in this version we are dealing with a Kharash reaction and not a Wurtz reaction. However, it is still not clear to what extent such admixtures can distort the results discussed above.

It is interesting that monobromonorcarane was obtained in high yield in the reaction of 7,7-dibromonorcarane with methylmagnesium bromide in THF,[29] which makes it possible to employ RMgX in such systems as a reducing agent for preparative purposes.

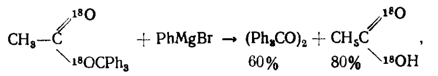
It is appropriate to mention here the reaction of organomagnesium compounds RMgBr (R = Ph, $PhCH_2$, or n-Bu) with (trichloromethyl)carbinyltoluene-*p*-sulphonates $\mathrm{R'-\underset{\underset{OTos}{|}}{C}HCCl_3}$ (R' = Alk or Ar) in ether, for which a free radical mechanism has been proposed[30]. The reaction results in a mixture of products, the composition of which in each specific case depends on the nature of RMgBr and the toluene-*p*-sulphonate derivative. For example, when R = R' = Ph, the products are *ββ'*-dichlorostyrene (78%), benzene (64%), styrene (42%), and ethyl *α*-phenylethyl ether (13%). In the presence of benzylmagnesium bromide, the corresponding ether was not detected, but bibenzyl was formed in a quantitative yield. The authors believe that the first reaction stage involves electron transfer:



$$\mathrm{RMgBr + R'\underset{\underset{OTos}{|}}{C}HCCl_3 \rightarrow R^{\cdot} + R'\underset{\underset{OTos}{|}}{C}H\dot{C}Cl_2 + MgBrCl + TosMgCl.}$$

All the products detected have been accounted for by further reactions of the above radicals (including their reactions with ether). The formation in the initial reaction step of the radical $R'CHCCl_3$ appears to be no less likely and its further reactions (together with those of R·) should naturally lead to the same composition of the products.

A mechanism including a reaction transfer stage has also been proposed for the reaction of phenylmagnesium bromide with triphenylmethyl acetate in ether, which proceeds in an unusual manner[31]. The use of acetate labelled with ^{18}O shows that the entire label passes to acetic acid:



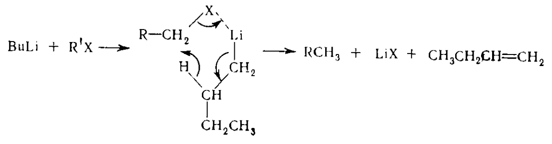
i.e. the reaction takes place with dissociation of the $O-CPh_3$ bond. Apart from trityl peroxide and acetic acid, acetophenone (14%), benzophenone (12%), triphenylmethane (23%), biphenyl (23%), and triphenylmethanol (about 5%) were detected in the reaction products.

III. REACTIONS WITH ORGANOSODIUM AND ORGANOLITHIUM COMPOUNDS

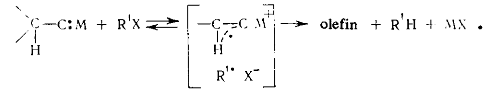
Ideas concerning the mechanism of the classical Wurtz reaction between RNa or RLi and R'X have undergone approximately the same development. In 1927 Marvell et al.,[32] who investigated the reaction of butyl-lithium with a wide variety of halogeno-derivatives, showed that the yield of RR' varies within very wide limits as a function of the nature of R'X. In many cases hydrocarbons of the type R'R' were isolated together with RR'. Thus *trans*, *trans*-1,4-diphenylbuta-1,3-diene was obtained together with 1-phenylhex-1-ene in the reaction involving *α*-bromostyrene. The authors showed that it is formed from the radical $PhCH{=}\dot{C}H_2$ and not as a result of exchange and subsequent recombination processes. This conclusion is based on the fact that the reaction with almost all the R'X was accompanied by the appearance of a colour (particularly pronounced for *α*-bromostyrene and chlorotriphenylmethane), which disappeared at the end of the reaction. The reaction of Ph_3CCl led to the formation of triphenylmethyl peroxide together with 1,1,1-triphenylpentane. An unexpected result, which is difficult to account for by differences in the structures of the R'X, was obtained in the reaction of butyl-lithium with isomeric bromotoluenes. For *p*-$BrC_6H_4CH_3$, the product of the Wurtz reaction was obtained in 76% yield, while the *m*- and *o*-isomers give almost quantitative yields of toluene.

We may note that, in the early studies on the Wurtz reaction as well as in the studies published much later than the investigation described above, the formation of products of the disproportionation of RH, R'H, R(–H), R'(–H), and (or) the symmetrical hydrocarbons R'_2 and R_2 was frequently observed together with that of the recombination product RR', but the possibility of a radical mechanism was either not discussed or was frequently ruled out on *a priori* grounds. For example, Morton et al.[33] stated that all the recombination and disproportionation products in the reactions of R'X with RNa can be explained without resorting to the hypothesis of the existence of radicals (although they did not rule out completely the possibility of a free radical pathway). Incidentally the conclusion that the hydrocarbons RH and R(–H) are not formed as a result of the disproportionation of radicals was based on the finding that in the reactions investigated the yield of RH as a rule greatly exceeded the yield of R(–H). Many other investigators also hold the view that the Wurtz reaction has an ionic mechanism (see, for example, Refs. 7 and 34–38). The stereochemical data discussed below constitute an important argument in this connection.

Defending the ionic reaction mechanism, Eastham and Gibson[39], wrote that the formation of the alkane RH and the alkene R(–H) does not by itself demonstrate the existence of the radical R·, i.e. it is the result of the hydride reduction of R'X by the *β*-hydrogen atom of the RM molecule and not of the disproportionation of the radical. In the reaction of butyl-lithium with 2-bromo-octane in hexane, which they investigated, octane (66%) and dodecane (32%) are formed, while in the reaction with bromocyclohexane the products are cyclohexane (56%), butylcyclohexane (32%), and cyclohexene (5%). Under these conditions, other halogeno-derivatives—1- and 2-chloro-octanes, 1-chloroisopentane, 4-chloroheptane, and fluoro- and chloro-cyclohexanes—were also reduced to alkanes. Using butyl-lithium labelled with tritium in the *β*-position, the authors obtained tritiated cyclohexane, which enabled them to suggest a mechanism for the reduction of halogeno-derivatives by the *β*-hydride atom of butyl-lithium:

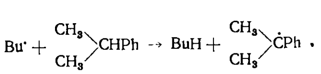


However, from our point of view, the hydride shift can also occur as a multistage process including an electron transfer stage:



This conclusion was based on the observation of the CIDNP of the methine proton of triphenylmethane in the reaction of Ph_3CX (X = Cl, Br, or ClO_4) with di-n-butyl or di-s-butyl-mercury and also with triethylsilane. In this case the results do not rule out the SET mechanism, which we believe can be invoked to account for the ease of reduction by metal hydrides of the C–Hal bond involving a bridgehead halogen[41]. We may note that Jefford et al.[41] assume that the reaction takes place as a result of cationoid abstraction of the halogen and the protonation of the resulting carbanion by the solvent.

Some evidence for the formation of radicals in the Wurtz reaction was obtained by Bryce-Smith[42]. He used cumene as a trap for the butyl radical formed in the reaction of the butyl derivatives of lithium and sodium with butyl halides:

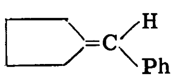


$$Bu^{\cdot} + (CH_3)_2CHPh \rightarrow BuH + (CH_3)_2\dot{C}Ph \ .$$

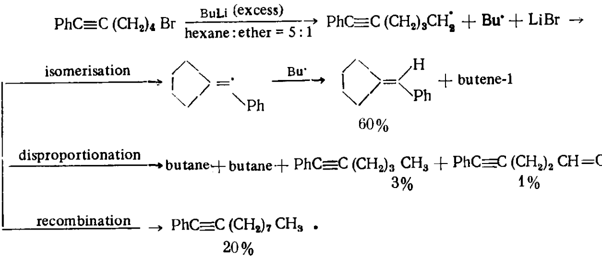
The resulting radical then dimerises to 2,3-dimethyl-2,3-diphenylbutane.

Sauer and Braig[9] also considered electron transfer as the first stage of the Wurtz reaction and showed that the reaction of 2-bromo-octane with allyl-lithium in ethyl ether or TMF (at 0°C) gives an 87–95% yield of the corresponding hydrocarbon RR′ and only trace amounts of octane, octene, and 7,8-dimethyltetradecane. The addition of cumene has no influence on the reaction. However, the interaction of the same bromide with ethyl- or n-propyl-lithium (at 0° or 35°C) leads to the formation of a mixture of the hydrocarbons R′H, R′(–H), RR′, and R′R′ in the proportions (0.6–0.9) : (0.6–0.9) : 1.0 : (0.5–0.6). When cumene is added, about 8% of bicumenyl is formed. According to the authors[9], the products detected are formed via the recombination or disproportionation of the radicals $R^{\cdot}$ and $R'^{\cdot}$ arising in the primary reaction step.

The possibility of a radical mechanism sometimes assumes special interest, for example in the reaction of $PhC{\equiv}C(CH_2)_4Br$ with BuLi, which leads to the cyclisation product[43,44]



Kandil and Dessy[43] suggested that it is formed as a result of the anionic cyclisation of the corresponding organolithium compound $PhC{\equiv}C(CH_2)_4Li$, arising in the exchange reaction. Ward[44] adduces convincing data in support of a radical mechanism of the cyclisation reaction:



Similar results have been obtained with ethyl- and t-butyl-lithium.

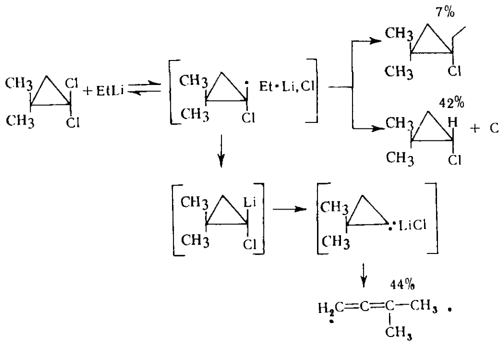
Direct detection of radicals by ESR in the reaction of ethyl-lithium with chlorotriphenylmethane was achieved by Shilov et al.[45] The concentration of triphenylmethyl radicals exceeded the equilibrium value, which undoubtedly indicated an SET mechanism. Ethane and ethylene were formed from methyl radicals; however, the absence of deuterium from ethane when the reaction was carried out in a deuteriated solvent forced the authors to assume that the ethyl radicals do not exist as kinetically independent species and that a complex with EtLi is formed in which disproportionation takes place. Ward[46] believes that there is a relation between the complex formation process and the state of aggregation of the organolithium compounds in solution.

Proof of the formation of radicals in the primary reaction step was obtained for simple alkyl halides by D'yachkovskii and Shilov[47] in a study of the reaction of ethyl-lithium with ethyl iodide, the products of which were ethane, ethylene, and butane, ethylene being formed according to the authors on disproportionation of the radical $R^{\cdot}$ in the cage. The relative yield of ethane decreased when the reaction was carried out in decalin with added anthracene and also in benzene and toluene, which are known to be capable of interacting with alkyl radicals. The relative yield of ethane falls even more when α-methyl-styrene is added to decalin (by a factor of ten compared with the yield of ethane in pure decalin). When experiments in deuteriated solvents were carried out, monodeuteroethane was detected: 2.3% in C_6D_6, 3% in C_6D_{12}, and 5.6% in $C_6D_5CD_3$.

A radical mechanism may also be considered for the exchange reaction between RLi and R′X. The exchange reactions of PhI with RLi, where R = alkyl, cycloalkyl, alkenyl, or aryl, have been used by Applequist and O'Brien[48] to estimate the relative stabilities of various compounds RLi (i.e. the stabilities of the carbanions), and data for the equilibrium positions in the system served as a basis for a method of determining the pK_a values for CH acids[49]. It has been suggested that the reaction is electrophilic. According to Wittig[50], the main argument has been the ease of carrying out this reaction with bromo-derivatives of bicyclic compounds containing bridgehead bromine, for example bromotriptycene, for which S_N2 and S_N1 reactions are hindered or even impossible. According to Wittig, the electrophilic attack is preceded by the nucleophilic attack of R^- on the bromine, which then expands its electron shell to a decet. Other investigators[51] also support the view that the exchange processes are heterolytic. However, the ease of exchange in such systems does not conflict with a radical mechanism, including SET, either.

Evidence for the radical mechanism of the exchange reaction was obtained with the aid of CIDNP studies[52–57]. Thus Ward and Lawler[52] observed the polarisation of protons in the but-1-ene and isobutene formed in the reaction of n-butyl-lithium and t-butyl-lithium with butyl bromide in hexane. The octane formed is probably also polarised, but the observation of the polarisation is hindered by the superposition of the signal due to the solvent and the reactants. In the almost "pure" exchange reaction between ethyl-lithium and iodobenzene[53] the methylene proton of the ethyl iodide formed in 80% yield are polarised. Similar results were obtained in a study of the reaction of ethyl iodide with ethyl-lithium (in benzene at 40°C), where the polarisation of the methyl and methylene protons of the ethyl iodide formed in the course of the exchange was observed[53]. Both iodides (s-BuI and n-BuI) were polarised in the reaction of n-BuLi with n-butyl iodide in consequence of the reversibility of the reaction. A similar situation was observed in the converse exchange reaction—the reaction of s-butyl-lithium with n-butyl iodide[53]—and in the reaction of n-butyl-lithium with n-butyl iodide and isopropyl iodide, where the vinyl protons of propene and but-1-ene were found to be polarised[54]. We may note that the polarisation of the protons in the molecule of the organolithium compound has not been observed in any of the reactions, in agreement with the data of

Shilov et al.,[45] showing the absence of ethyl radicals in the reaction of ethyl-lithium with chlorotriphenylmethane. Positive CIDNP has been observed in the products of the reaction of ethyl-lithium with 1,1-dichloro-2,2-dimethylcyclopropane[58], i.e. in 3-methylbuta-1,2-diene and 1-chloro-2,2-dimethylpropane.



Several instances of the observation of CIDNP in the products (RR′) of the Wurtz reaction proper, for example in the reaction of ethyl-lithium with *αα*′-dichlorotoluene[59], are known. This example is of interest, because it has been used to demonstrate the dependence of the observed polarisation of *α*-chloro-*α*-phenylpropane on the applied magnetic field. Polarised ethane was formed in the reaction of ethyl iodide with sodium in dimethoxyethane (DME), which enabled the authors[60] to treat the reaction of CH_3I with CH_3Na as a radical process; however, the polarisation of cyclobutane in the analogous reaction of 1,4-diiodobutane with sodium could not be observed.

The CIDNP of ^{19}F has been observed in the products of the reaction of n-butyl-lithium with *p*-fluorobenzyl chloride[56,57] and pentafluorobenzyl chloride[57]; in both cases, the reaction products are the corresponding symmetrical diphenylethanes and phenylpentanes (the product ratio $R'_2 : RR' = 1:5$ for the former reaction and 1 : 6 for the latter, as shown by the NMR spectra); intense polarisation was observed for both products[56]. The *p*-nitrobenzyl radical has been detected in the reaction of BuLi with *p*-$NO_2C_6H_4CH_2Cl$.[57]

A not altogether comprehensible result was obtained in a study by Ward[46], who showed that there is no polarisation in the exchange reaction in the t-BuLi–n-BuLi system at −70°C, but on raising the temperature CIDNP is observed in the recombination and disproportionation products. However, in the EtLi–iso-PrI system at 40°C both iodides (EtI and iso-PrI) are polarised, undoubtedly due to the exchange process, which Ward treats as the interaction of R· and R′I, in conformity with Russell's mechanism (see below).

The observation of the polarisation of all the products formed in the reaction of RLi with R′X (the metal–halogen exchange, the "normal" Wurtz reaction, and the formation of radical disproportionation products) makes it possible to describe all these processes in terms of the SET mechanism.

Russell[61], who succeeded in showing that one electron transfer may occur in the Wurtz and exchange reactions even when the yield of RR′ is fairly high, attributes a general significance to this mechanism. In a study of the reaction of RLi with R′X by ESR using a flow system, whereby detection approximately 0.03 s after mixing the reactants is possible, Russell obtained direct proof of the primary formation of radicals. In the reactions of n-butyl-lithium with R′I (R′ = Et, n-Pr, n-Bu, n-Oct, or t-Bu), only the R′· radicals, which arise before the metal–halogen exchange takes place, i.e. from the iodide molecule, were observed. However, the spectra of certain bromides and $PhCH_2Cl$ revealed only the signal of the n-butyl radical, while both possible radicals were found in the reaction of s-BuLi with EtBr and of n-BuLi with CH_3I.

According to Russell, the results agree best with the following mechanism

$$RM + R'X \xrightarrow{k_1} R^{\cdot} + R'^{\cdot} + MX; \qquad (1)$$

$$R^{\cdot} + R'X \xrightarrow{k_2} RX + R'^{\cdot}; \qquad (2)$$

$$R'^{\cdot} + RLi \xrightarrow{k_3} R'Li + R^{\cdot}; \qquad (3)$$

$$R'^{\cdot} + R^{\cdot} \xrightarrow{k_4} \text{alkanes and alkenes.} \qquad (4)$$

The particular radical detected in the spectrum depends on the rates of stages (2) and (3). On the other hand, the rates are naturally determined by the nature of the radicals R· and R′· and the anion X^-. For iodides (R = Bu and R′ = Et or Pr), the rate of stage (2) exceeds that of stage (3) and the radicals R′· have been observed. When $X^- = Br^-$ or Cl^-, the rate of this stage diminishes and only R· or a mixture of R· and R′·¶ ($k_2 \simeq k_3$) is observed. For allyl bromide, the spectrum reveals the presence of allyl radicals only. Russell states that reactions (2) and (3) constitute the possible mechanism of the metal–halogen exchange. However, he does not rule out the possibility of some contribution by the heterolytic process in such reactions.

It is seen from the examples quoted that the composition of the products formed depends on the nature of R, R′, X, and M. The result is determined to a significant extent by the nature of the solvent. In the study of Eastham and Gibson[39] already mentioned, it was shown that in a non-polar medium (hexane) butyl-lithium reacts with R′X via a hydride reduction mechanism, while in ether the usual Wurtz reaction takes place. The change in the mode of reaction as a function of the nature of the solvent has been illustrated[63] by a study of the reaction of butyl-lithium with benzyl chloride. In hexane and ether, the authors observed the formation of n-alkylbenzene and bibenzyl, while in THF *trans*-stilbene was found (20%). A significantly higher yield of the dimerisation products RR′ in the Wurtz reaction has been observed in benzene in relation to ether[64]. However, an increase in solvent polarity usually leads to an increase of the yield of the Wurtz reaction product. Thus it has been shown in a recently published study[65] that in the hexane : THF = 1 : 5 mixture the reaction of n-butyl-lithium and n-octyl-lithium gives satisfactory yields of the hydrocarbons RR′ even with aryl halides.

¶ The problem of the mechanism of the reaction between R and R′X can also be treated from different standpoints: as an S_N2 reaction involving the halogen atom or as the reduction reaction

$$R^{\cdot} + R'X \longrightarrow R^{+} + (R'X)^{\overset{\cdot}{-}} \longrightarrow RX + R'^{\cdot},$$

which naturally proceeds more readily with iodides. The results agree with those of Evans and Szwarz[62], who showed that the methyl radical abstracts the halogen from MeI 7 × 10^3 faster than from MeBr. This also applies to the reaction of R′· with RLi.

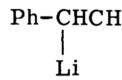
By tradition it has come to be accepted that an increase in the polarity of the C–M bond under the influence of the solvent facilitates the heterolytic process, which is indicated by the increase of the yield of RR′, and that the radical mechanism can be replaced by a heterolytic mechanism under the influence of the solvent[45,66–68]. Thus a detailed study has been made[66] of the reaction of butylmagnesium iodide with R′X in cumene or in higher alkanes and it has been shown that the hydrocarbons RH, R′H, R(–H), and R′(–H) are formed in all cases, while in cumene the formation of appreciable amounts of bicumenyl is observed in addition. On passing to DME, the situation changes sharply. The simplest RMgX and R′X readily enter into the "normal" Wurtz reaction in DME, although even in ether this reaction is not at all characteristic of these substances. The authors believe that, on passing from hydrocarbon solvents to DME, the mechanism of the reactions of organomagnesium compounds with R′X changes from radical to heterolytic.

Here one should note that the exchange reaction R′X + RM → R′M + RX, which is well known for the more reactive organolithium compounds, is believed to be generally atypical in the series of organomagnesium compounds and takes place only when the difference between the electronegativities of the groups R and R′ is large[21]. However, in strongly solvating solvents such radical exchange does occur also for the simplest alkyl or aryl-magnesium halides and alkyl halides[67]. For example, the degree of exchange in the reaction of n-$C_5H_{11}MgBr$ with CH_3I varies from 5.7% (1 h, 0°C, in ether) to 38% in DME. Since the ease of exchange increases with increase of the solvating capacity of the solvent, the authors treat this reaction as heterolytic. However, one cannot rule out the possibility that not only the amount of ionic character of the C–M bond but also the ability of the organometallic compounds to behave as an electron donor is altered by the solvent. From the standpoint of the unified SET mechanism, the influence of the solvent on the composition of the products (but not on the rate of reaction) should be manifested as a result of a change in the nature of the "cage" enclosing the radical-ion pairs formed and not as a result of the change in the nature of the dissociation of the C–M bond. Unfortunately, nothing is as yet known about the nature of this cage and about its influence on the stability of the radical-ion pair.

Thus, in recent years, particularly after the publication of CIDNP data and Russell's study[61] concerning the detection of radicals in the reactions of simple alkyl halides with alkyl-lithium, there has been a tendency to treat the exchange and Wurtz reactions from the standpoint of the radical mechanism. However, we believe that the conclusion that there is a single mechanism for all the processes involving the SET stage may prove to be premature. We have been led to this conclusion mainly by analysis of stereochemical data.

IV. STEREOCHEMISTRY OF THE EXCHANGE AND WURTZ REACTIONS

In the first place we shall consider the results obtained in the study of the stereochemistry of the exchange reactions. Unfortunately the stereochemistry of such processes, occurring at a tetrahedral unstrained carbon atom, has been hardly investigated. The only available stereochemical result for reactions of this kind is apparently the partial retention of configuration found by Letsinger in the s-butyl-lithium–optically active 2-iodo-octane system[69]. Only when the reaction was carried out at −70°C (in a petroleum ether–ethyl ether mixture) was the author[69] able to obtain the optically active 2-lithio-octane, but its activity was lost on raising the temperature to 0°C (after carboxylation, the acid proved to be fully racemic).

One cannot rule out the possibility that the racemisation of the organometallic compounds formed in the metal–halogen exchange in fact accounts for the formation of the racemic products RR′ in the reactions of R′Hal with simple alkyl derivatives of metals (see below), particularly if one bears in mind that the reactions are frequently carried out at fairly high temperatures (0°C and above). For example, Wittig[70] obtained virtually inactive 2,3-diphenylbutane in the reaction of the optically active α-bromoethylbenzene with phenyl-lithium in ether and explained its formation by the exchange reaction of the bromide with PhLi and the subsequent Wurtz reaction between  $\mathrm{Ph{-}\underset{\underset{\textstyle Li}{|}}{C}HCH_3}$ and $PhCH(Br)CH_3$. Thus, in principle, the reaction can take place with retention of configuration. The possibility of the retention of configuration in the metal–halogen exchange reaction has been confirmed also by the finding that the exchange takes place readily between 1-bromotriptycene and butyl-lithium (with formation of 1-lithiotriptycene)[50], i.e. in the system where the retention of configuration is predetermined by the structure of R′X and where processes of the S_N2 type, occurring with retention of configuration, are impossible.

The organolithium derivatives of the vinyl and cyclopropyl series are more stable, so that the stereochemistry of the metal–halogen exchange in such cases has naturally been investigated in greater detail. The organolithium compounds were not isolated or a configuration assigned in any instant and the stereochemical course of the reaction was inferred from the configuration of their conversion products, for example after carboxylation, Li–H exchange, the cleavage of $HgCl_2$, I_2, or Br_2, etc. (it is assumed that all these reactions are of the S_N2 type and take place with retention of configuration). Thus investigations have shown that all the reactions investigated take place with retention of configuration (Table 1), which is evidence against the involvement of free radicals in the exchange reactions. The retention of configuration in the exchange reactions of the *cis*- and *trans*-isomers of the cyclohexyl derivatives of lithium with methyl iodide and bromobenzene[71] also supports these conclusions.

We shall now consider the stereochemical data available for the Wurtz reactions involving organosodium, organolithium, and organomagnesium compounds. The results are compiled in Tables 2–4. The principal stereochemical results in Tables 2–4 may be summarised as follows. The reactions of organosodium and organolithium derivatives of the benzyl and allyl type with R′X proceed with preferential and sometimes complete inversion of configuration. However, in the reactions of the corresponding organomagnesium compounds, the percentage racemisation increases appreciably. On the other hand, the interaction of simple alkyl derivatives of sodium and lithium with RX′ results in racemisation, the only exception apparently being the reaction of lithium diphenyl cuprate with s-butyl bromide, which takes place with inversion of configuration to the extent of 84–92%†.[81]

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† Naturally the mechanisms of the reactions of Ph_2CuLi and simple RLi and RNa with R′X are the same.

From general considerations, the stereochemical results of radical reactions presumably involve racemisation, possibly with partial retention of configuration. The retention of configuration under these conditions may be due to the recombination of radicals in the cage or the presence of a barrier to inversion. Only in the case of a stable radical, with a fairly high inversion barrier, can one expect the preferential retention of configuration. This probably actually accounts for the observed retention of configuration in the reaction of bromo-derivatives of the vinyl series with lithium dimethyl- or diphenyl-cuprates[81,82].

Table 1. Stereochemical results of the reactions of RLi with R'X.

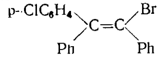
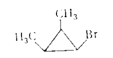
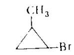
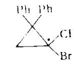
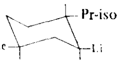
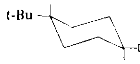
RLi	R'X	Stereochemical result	References
s-BuLi	2-IC_8H_{17}	20% retention, 80% racemisation	69
n-BuLi	*cis-* and *trans-*  $p\text{-}ClC_6H_4(Ph)C{=}C(Br)Ph$	retention	72
»	*cis-* and *trans-* $PhCH{=}C(Br)Ph$	retention	73, 74
»	*cis-* and *trans-* 	retention	75
	cis- and *trans*	retention	76
»			
»			
	CH_3I	90% retention	71
	PhBr	85% retention	71
			

Table 2. Stereochemical results of the reactions of RNa with R'X.

RNa	R'X	Yield of RR', %	Stereochemical result	References
C_2H_5Na	2-BrC_8H_{17}	25	90% racemisation	35
n-C_4H_9Na		35	total racemisation	36
2-NaC_8H_{17}		—	ditto	37
s-C_4H_9Na	s-C_4H_9Br	—	"	37
C_2H_5Na	2-ClC_8H_{17}	—	inversion, 20% racemisation	77
2-NaC_8H_{17}	»	—	partial inversion, exact assignment of configuration unavailable	37
Ph_2CHNa	$PhCH(Cl)CH_3$	—	exact assignment unavailable, but only slight racemisation observed	78
$PhCH_2Na$	s-C_4H_9Br	65—69	74% inversion, 26% racemisation	5
»	2-BrC_8H_{17}	80	70% inversion, 30% racemisation	5
$CH_2{=}CHCH_2Na$	»	83	79-81% inversion, 13-21% racemisation	6
»	$PhCH(Cl)CH_3$	—	inversion (exact assignment unavailable)	79
$NaCH(COOEt)_2$	2-BrC_8H_{17}	—	inversion	34

Naturally the inversion of configuration cannot be interpreted from the standpoint of the radical mechanism. For this purpose, one would have to postulate the occurrence of S_N2 reactions which would result in inversion of configuration and which would include attack by $R^{\cdot}$ on the carbon atom:

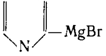
$$R^{\cdot} + R'X \rightarrow RR' + X^{\cdot}.$$

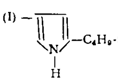
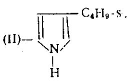
Table 3. Stereochemical results of the reactions of RLi with R'X and of R_2CuLi with R'X.

RLi or R_2CuLi	R'X	Yield of RR', %	Stereochemical result	References
n-C_4H_9Li	s-C_4H_9Br	37	98% racemisation	80
PhLi	2-BrC_8H_{17}	30	racemisation	9
n-C_3H_7Li	»	30	racemisation	9
$PhCH_2Li$	s-C_4H_9Br	58	100% inversion	7
»	2-BrC_8H_{17}	85	ditto	7
$CH_2{=}CHCH_2Li$	»	68	108% inversion	
»	»	87—95	inversion	9
»	2-ClC_8H_{17}	59	92% inversion	7
»	$PhCH(Cl)CH_3$	34—39	29-38%* inversion	7
Ph_2CHLi	2-ClC_8H_{17}	48	100% inversion	7
$CH_2{=}CHCH_2Li$	2-$C_8H_{17}SO_3C_6H_4CH_3$	60	93% inversion	8
»	2-IC_8H_{17}		90% inversion	
$PhCH_2Li$	»		90—93% inversion	8
»	2-$C_8H_{17}SO_3C_6H_4CH_3$		90-93% inversion	
Ph_2CuLi	s-C_4H_9Br		84-92% inversion	81
»	*cis-* and *trans*-bromostyrenes	98	retention	81
$(CH_3)_2CuLi$	*trans*-bromostyrene	81	retention	82
»	*cis*-bromostyrene	»	retention	
»	*cis*-1-bromo-4-t-butyl-cyclohexane	45% *trans*- 41% *cis*-	non-stereospecific	82

* The authors believe that the low percentage inversion may be due to the metallation of the hydrocarbon RR' and the racemisation of the carbanion.

Table 4. Stereochemical results of the reactions of RMgX with R'X.

RMgX	R'X	Yield	Stereochemical result	References
CH_3MgI	$PhCH(Cl)C_2H_5$	—	racemisation	83
$CH_2{=}CHCH_2MgBr$	2-BrC_8H_{17}	78	79-87% inversion, 13-21% racemisation	6
»	$PhCH(Cl)CH_3$	—	low percentage inversion, exact assignment unavailable	79
$PhCH(MgCl)CH_3$	$PhCH(Cl)CH_3$	—	racemisation	84
$PhCH_2MgCl$	2-BrC_8H_{17}	17	91% racemisation	6
	s-C_4H_9Br	30% (I)* 12% (II)	100% inversion	85

* (I) —  ; (II) — 

Furthermore, it is known[79] that such processes involve as a rule terminal atoms [Hal, M(I)]:

$$R^{\cdot} + R'X \rightarrow RX + R'^{\cdot}.$$

This stereochemical result of the reactions of RNa with R'X in fact forced Le Goff et al.[34] to conclude as early as

1958 that "there is almost no doubt about the ionic mechanism of the reaction".

Another stereochemical result, namely racemisation, which has been observed for many reactions of RLi and RNa with **R'X**, can be interpreted fairly simply by the radical mechanism. However, in this case there is a possibility also of an alternative explanation associated with the occurrence of metal–halogen exchange processes. One may suppose that the exchange processes involving simple alkyl derivatives of lithium and sodium proceed more readily than for the benzyl or allyl derivatives and this is the reason for the formation of the racemic products **RR'** (RLi or RNa, formed as a result of the exchange reaction, racemise; see above). On the other hand, if it is assumed that the exchange processes proceed via a radical mechanism, then evidently they must be accompanied by "losses" associated with the reactions of the radicals liberated from the cage. Indeed the yields of **RR'** are extremely low in the reactions of **R'X** with simple alkyl derivatives of lithium and sodium, while in the case of the allyl and benzyl derivatives they are nearly quantitative. However, it is at present extremely difficult to reach any conclusions, since an increase in the reactivity of RM, like that of **R'X** (for example on passing from chlorides to iodides), should increase the rates of both processes (although possibly to different extents).

On the other hand, it is difficult to account for data obtained for the Wurtz reactions involving RMgX from the standpoint of an ionic S_N2 mechanism. Exchange processes are known to be less typical for organomagnesium compounds than for organolithium or organosodium compounds[21,67]. Nevertheless, preferential racemisation, even in reactions with **R'X** incapable of reacting via the S_N1 mechanism although the yield of **RR'** are in fact highest in processes of this type, is often the stereochemical result of reactions involving allyl- or benzyl-magnesium halides. It is noteworthy that the available data for the stereochemistry of the Wurtz reaction with participation of RMgX are limited to only a few examples (Table 4).

It is evident from the data described that the Wurtz reaction and the metal–halogen exchange reaction cannot be described within the framework of a single mechanism, particularly since a change in the nature of M, R, R', and the halogen may alter the process mechanism. We shall now consider the possible mechanisms of the exchange and Wurtz reactions in the light of the available data (particularly stereochemical data) for these processes.

V. POSSIBLE MECHANISMS OF THE EXCHANGE REACTIONS

1. The mechanism proposed by Wittig to explain the ease of the exchange of the bridgehead halogen[50], which involves nucleophilic attack on the halogen (cationoid abstraction of the halogen) and which may be regarded as a mechanism involving electrophilic substitution at the carbon atom in **R'X**:

$$R'X + RM \rightarrow [R'\!:\ddot{X}\!:\ \,:\!R]^{-}M^{+} \rightarrow RX + R'M.$$

The stereochemical result of such a process should be retention of configuration. This mechanism is frequently invoked, particularly for reactions of organobimetallic compounds with **R'X**, to explain the retention of configuration in exchange reactions. However, exchange processes are as a rule accompanied by the formation of alkanes and alkenes, which cannot be explained within the framework of this mechanism (provided, of course, that the exchange reactions and the reactions involving the formation of these hydrocarbons have a common rate-limiting stage).

2. Electron transfer with formation of a radical-ion pair in which a redistribution of radicals may occur:

$$RM + R'X \rightarrow \begin{bmatrix} R^{\cdot} & M^{+} \\ R'^{\cdot} & X^{-} \end{bmatrix} \rightarrow RX + R'M.$$

The formation of alkanes (RH, and R_2 or R'_2) and alkenes can be explained from the standpoint of this mechanism by the liberation of $R^{\cdot}$ and $R'^{\cdot}$ radicals from the cage. If it is postulated that the radical distribution process takes place in the cage, one can thus account for the observed retention of configuration. However, in consequence of the inversion of the radicals in the cage, even in this case the process can occur with partial or even preferential racemisation.

3. The radical chain mechanism proposed by Russell[61]:

$$R^{-}M^{+} + R'X \rightarrow R^{\cdot} + R'^{\cdot} + MX; \tag{1}$$

$$R^{\cdot} + R'X \rightarrow RX + R'^{\cdot}; \tag{2}$$

$$R'^{\cdot} + RM \rightarrow R'M + R^{\cdot}; \tag{3}$$

$$R^{\cdot} + R'^{\cdot} \rightarrow RR' + \text{alkanes and alkenes.} \tag{4}$$

This mechanism probably gives at the present time the best explanation of the exchange process [stages (2) and (3)]. The formation of different hydrocarbons can be understood within the framework of this mechanism, although the stereochemical result of reactions (2) and (3) should be racemisation. In a few instances one can probably expect also the retention of configuration, for example for radicals of the vinyl and cyclopropyl series which have high inversion barriers. There is no doubt that the free-radical mechanism appears particularly attractive for the exchange reaction, which is in essence an oxidation-reduction process. However, one cannot explain within the framework of this mechanism the results of Mechinger's study, which has become a classical (and so far unique) example of this kind, showing the possibility, in principle, of the retention of the stereochemical configuration in exchange reactions involving an sp^3-hybridised uncharged carbon atom[69]. On the other hand, the observation of CIDNP in alkyl halides together with the observation of the polarisation of alkanes and alkenes shows that these products are formed via a mechanism involving an SET stage or a chain radical process. There remains only one possibility—to assume that in reality a combination of mechanisms [(1) and (2) or (2) and (3)] obtains. There has been only one investigation which throws doubt on the SET mechanism of radical exchange reactions (in halogen–metal systems). This is the study of Ward and coworkers[46] (whose results have been published in the abstracts of reports at the conference in Belgium in 1971), where the authors failed to observe CIDNP in the reaction of t-BuLi and n-BuI at −70°C involving exchange, but did observe CIDNP in the disproportionation products formed on raising the temperature, i.e. in the products arising under the conditions of the Wurtz reaction.

VI. POSSIBLE MECHANISMS OF THE WURTZ REACTION

1. The heterolytic mechanism of the S_N2 type[‡]

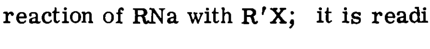
$$RM + R'X \rightarrow [M^{\delta+}R^{\delta-} \ldots R'^{\delta+}X^{\delta-}] \rightarrow MX + RR'.$$

The stereochemical result of this process is inversion of configuration. This mechanism has been frequently invoked in studies on the reactions of benzyl and allyl derivatives of lithium and sodium, since preferential inversion of configuration has in fact been observed in such cases. The reactions of lithium dimethyl- and diphenyl-cuprates with R'X also take place with inversion of configuration[81,82], probably owing to their pronounced nucleophilic properties in relation to the carbon atom.

This mechanism is probably also valid for the reactions of simple alkyl derivatives of sodium and lithium with R'X, which take place with racemisation, if it is assumed that the racemisation is a result of the loss of configuration by the organometallic compound RM during the exchange process and is not a consequence of the Wurtz reaction. This hypothesis is particularly likely, because simple alkyl derivatives of lithium and sodium should show the greatest tendency towards exchange reactions by virtue of their basicity, which is confirmed by the formation of R_2 and R_2' together with RR' in these reactions, in contrast to the reactions of benzyl and allyl derivatives of sodium and lithium, where compounds RR' are sometimes formed in nearly quantitative yields. However, the stereochemical result (racemisation) in the reaction of optically active R'X with RMgX (even of the allyl and benzyl types) remains inexplicable within the framework of this mechanism. Exchange processes are not characteristic of these reactions, because the latter have been carried out in hydrocarbon media or in hydrocarbon–ether mixtures, where hardly any exchange processes occur. Unfortunately the stereochemical data obtained for Wurtz reactions involving RMgX are extremely limited.

A change in the nature of R'X can lead to a change from an S_N2 to an S_N1 mechanism, which involves attack by RM on the carbonium centre of the carbonium ion R'^+ of the corresponding ion pair R'^+X^-. Racemisation accompanied by inversion of configuration when the ion pair is involved should be the stereochemical result of this reaction. However, one should recall that such reactions are usually carried out in ethereal solvents or in ether–hydrocarbon mixtures, which hardly promotes the ionisation of the R'X molecule and the operation of an S_N1 mechanism. On the contrary, an increase of the electron-donating capacity of the solvent (for example on passing from ether to DME of the glymes) promotes the ionisation of the organometallic compound molecule.

2. The mechanism of the S_Ni type:



$$RM + R'X \rightarrow \left[\begin{array}{ccc} R & — & M \\ & & \uparrow \\ R' & — & X \end{array}\right] \rightarrow \left[\begin{array}{ccc} R & \cdots & M \\ \vdots & & \vdots \\ R' & \cdots & X \end{array}\right] \rightarrow RR' + MX.$$

An attempt has been made to consider this mechanism for the Wurtz reaction of RNa with R'X; it is readily seen that it does not explain the formation of the observed products and stereochemistry, but it can obtain in reactions of covalent organometallic compounds, for example organomercury compounds (the reaction of RHgX or R_2Hg with R'X is discussed below). The stereochemical result of this reaction involves retention of configuration. However, when a fairly stable carbanion corresponds to the organic group R in the RM molecule, the rate-limiting stage of this process may become the ionisation of the RM linkage under the influence of nucleophilic coordination, i.e. the true mechanism is of the S_E1 type. The stereochemical result in this case may be racemisation, although one cannot rule out partial retention of configuration.

Finally one cannot rule out the possibility that both processes can involve electron transfer as a separate stage, which is rate-determining in an ionisation mechanism. The occurrence of SET in this instance would explain the formation of radicals in the reaction of Ar_2Hg with Ph_3CX (Beletskaya et al.[87]) and the CIDNP in the product Ph_3CCH_2Ar of the reaction of $(ArCH_2)_2Hg$ with Ph_3CX.[88] The stereochemical results of these reactions should involve retention of configuration or racemisation, but such data are so far unavailable in the literature.

3. Electron transfer as in the exchange reaction. When radicals recombine in the cage, one may expect the retention of configuration, but it is difficult to suppose that such recombination takes place only in the cage, particularly if one is dealing with fairly stable radicals of the allyl or benzyl type. On the other hand, one cannot explain within the framework of this mechanism the observed inversion of configuration which actually occurs in reactions involving RM of the benzyl or allyl type. The possible alternative explanation involving electron transfer in the oriented attack in the complex $[MR^{\delta-}\ldots R^{\delta+}{}'X]$[§] lacks any supporting evidence at the present time.

4. The radical chain mechanism in which the Wurtz reaction product is formed on recombination of the radicals R· and R'·. For the usual radicals, the natural stereochemical result should be racemisation. Analysis of the possible reaction pathways showed that, in order to account for the inversion of configuration in the Wurtz reaction, the absence of radical stages must be postulated.

At first sight the heterolytic mechanism in both the Wurtz and the exchange reactions is supported also by the finding that both reactions are appreciably accelerated in highly solvating media and that under such conditions the yield of hydrocarbons RH, R(–H), etc. is in fact reduced, while their amount increases sharply in hydrocarbon media, where there are virtually no products of the Wurtz reaction proper. These results can also be interpreted in a different way. An increase in the electron-donating capacity of the solvent leads to an increase of the basicity (and nucleophilicity) of the RM molecule and probably to a

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[‡] The assignment of this reaction to processes of the S_N2 type is purely arbitrary. It could be just as successfully regarded as a reaction of the S_E2 type. In this case the assignment was made because the study of the stereochemistry of the reaction (on which attention has been mainly concentrated in this section) has been carried out on the optical or geometrical isomers of R'X. This applies also to mechanisms of the S_Ni and S_Ei types.

[§] The formation of radicals has been recently demonstrated in a typical S_N2 reaction involving inversion of configuration. This enabled the authors to postulate that the transition state is a "hybrid" of the usual transition state of an S_N2 reaction and a radical pair[89]. On this hypothesis, it is indeed found that electron transfer should take place from "the rear". However, the authors failed to take into account the fact that a synchronous S_N2 mechanism cannot lead to the formation of different products (radicals and nucleophilic substitution products) from the same transition stage.

facilitation of the electron transfer process. On the other hand, these solvents can increase the stability of the radical-ion pair by solvation, as a result of which the radicals are less able to emerge from the cage.

Thus the observed characteristics of the Wurtz reaction cannot be explained within the framework of a single mechanism either. In order to account for the inversion of configuration, it is necessary to invoke a heterolytic pathway, while the retention of radicals (Russell's data[61]) and CIDNP in the recombination products requires a radical pathway. On the other hand, the ratio of the contributions of these pathways in each specific case constitutes an independent problem.

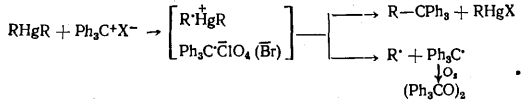
VII. REACTIONS OF OTHER ORGANOMETALLIC COMPOUNDS WITH ALKYL HALIDES

The formation of triphenylmethyl radicals has been demonstrated in a Wurtz-type reaction between organometallic compounds Ar_2Hg and triphenylmethyl bromide or perchlorate[87]. The ratio of the amounts of the Wurtz reaction products $ArCPh_3$ and triphenylmethyl peroxide depends strongly on the nature of the solvent and the substituent in the benzene ring of Ar_2Hg (Table 5).

Table 5. The yields of products in the reactions of Ar_2Hg with Ph_3CX.

p-X	Solvent	$(Ph_3CO)_2$, %	*p*-$XC_6H_4CPh_3$, %	*p*-X	Solvent	$(Ph_3CO)_2$, %	*p*-$XC_6H_4CPh_3$, %
H	benzene	15	85	CH_3O	DCE	90	10
H	DCE	60	40	Cl	»	20	80

In this case one can also postulate the occurrence of two simultaneous processes (radical and heterolytic), one of which may predominate. However, bearing in mind that the change in the rate of reaction following the alteration of X is described by the Brown–Okamoto equation (σ^+), the hypothesis of a single mechanism in which the rate-determining stage is electron transfer appears to be more probable:

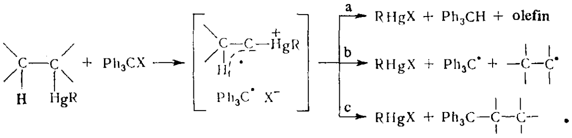


$$RHgR + Ph_3C^+X^- \rightarrow \left[\begin{matrix} R^{\cdot}\overset{+}{Hg}R \\ Ph_3C^{\cdot}\overline{C}lO_4\ (\overline{B}r) \end{matrix}\right] \rightarrow \begin{cases} R{-}CPh_3 + RHgX \\ R^{\cdot} + Ph_3C^{\cdot} \xrightarrow{O_2} (Ph_3CO)_2 \end{cases} .$$

One can attempt to explain the observed behaviour by the properties of the radical-cation formed initially, the stability of which should decrease in the sequence $CH_3O >$ H $>$ Cl; the higher the stability of these species the greater the "freedom" and ability to emerge from the cage acquired by its partner in the radical-ion pair, i.e. triphenylmethyl. On the other hand, the rate of reaction increases in the sequence methylene chloride $<$ CH_3CN $<$ benzene; the yield of triphenylmethyl peroxide increases in the same sequence. It may be that the radical-ion pair in π-donor solvents is more stable and this is responsible for the higher degree of recombination of the radicals in the cage; in the case of DCE, the radicals are more capable of leaving the cage (in all the solvents the formation of $Ph_3C^{\cdot}$ has been detected by ESR in the absence of oxygen, but in benzene the yield of the radical is low).

The validity of the proposed mechanism is demonstrated directly by the observation of CIDNP in $RCPh_3$ in the reaction of triphenylmethyl bromide with benzylmercury bromides p-$XC_6H_4CH_2HgBr$ (X = H or CH_3) and dibenzylmercury in DCE and methylene chloride[88].

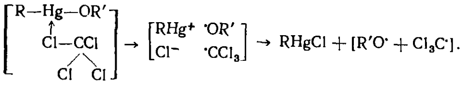
For alkyl derivatives of mercury containing a β-hydrogen atom capable of mobility as the hydride ion, the dominant mode of reaction with triphenyl methyl halides and perchlorates is known to be a hydride shift leading to triphenylmethane and not the formation of the Wurtz reaction products[90-92]. However, one may postulate that the elementary steps in the two outwardly different processes are of the same type. Indeed a considerable positive polarisation of the methine protons of triphenylmethane has been observed in the reactions of di-(n-butyl)- and di-(s-butyl)-mercury with Ph_3CX (X = Cl, Br, or ClO_4) in DCE.[93] On this basis, the following mechanism including the stage of one-electron transfer via the C–Hg bond to Ph_3CX has been postulated for the reactions under consideration:



In this mechanism triphenylmethane (pathway *a*) is a product of the abstraction of the β-hydrogen atom by the triphenylmethyl radical and not of the hydride shift as traditionally understood. The competing modes of reaction under these conditions are pathway *c* involving radical recombination in the cage and pathway *b* involving the liberation of the radicals from the cage, which becomes the main pathway when tri-(*p*-nitrophenyl)methyl bromide is used as the electrophilic agent (probably in consequence of the extremely high stability and low tendency towards recombination of the corresponding radical).

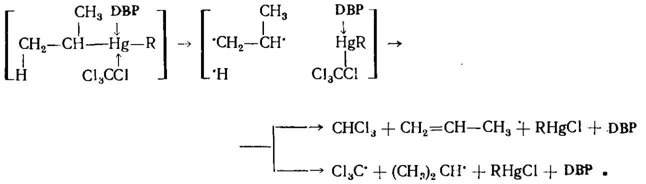
The SET mechanism in reactions of organomercury compounds with R′X may not be general and may obtain only in the specific case of the reaction with triphenylmethyl halides, owing to the ease of reduction of Ph_3CX and the formation of the stable triphenylmethyl radical. This hypothesis appears to be particularly valid, since in the general case the interaction of organomercury compounds with alkyl halides proceeds with extreme difficulty and a very low yield of RR′¶.

The mechanism including the SET stage has also been proposed for the reactions of mercury alkoxides RHgOR′ with polyhalogenomethanes and the reactions of dialkyl- and diaryl-mercury compounds with CCl_4 in the presence of di-t-butyl peroxide (DBP).[94] The organomercury compounds R_2Hg as a rule react with CCl_4 or $CHCl_3$ under severe conditions (heating to the decomposition temperature of R_2Hg) and the process has a free-radical mechanism. Following the replacement of R by an alkoxy-group, the reaction proceeds under milder conditions:



¶ This situation is analogous to that occurring in SN processes, where the usual SN2 reactions take place with inversion of configuration and cannot be simulated by the reaction of Ph_3CBr with t-BuO-(or PhO^-), which leads to radicals only[95].

DBP acts in the same way; its introduction into the reaction of alkyl or phenyl derivatives of mercury greatly accelerates the latter (the optimal conditions obtain when $R_2Hg:DBP = 1:1$). On the other hand, DBP itself is consumed in the reaction to an extent not greater than 5%. According to the authors[94], the catalytic role of DBP reduces to the formation of a complex with R_2Hg, as a result of which the Hg–C bond is polarised to such an extent that R_2Hg becomes reactive in relation to CCl_4. When CCl_4 reacted with Alk_2Hg in the presence of equimolar amounts of DBP, considerable amounts of chloroform and propene (more correctly, 1,1,1,3-tetrachlorobutane formed from propene after the addition of CCl_4) were found in the reaction mixture. The authors explain the formation of these products by an intermolecular hydride shift, which they believe also proceeds via an electron transfer stage:



However, the data quoted by the authors[94] do not show that this is the only reaction pathway.

The formation of racemic products in the reactions of phenyl- or α-naphthyl-cadmium chloride with α-bromopropionate esters and the observation of an intense signal in the ESR spectrum when the reactants are mixed, suggests that these reactions have radical mechanisms[96].

CIDNP (both emission and positive polarisation) has been recently observed in the reaction of ethyl-lead with hexachlorocyclopentadiene and hexachloroacetone (the solvents) at 140°C:[97]

$$Et_4Pb + C_5Cl_6 \rightarrow Et_3PbCl,\ EtCl,\ EtC_5Cl_5,\ C_5Cl_5H,\ C_2H_4,\ (C_5Cl_5)_2.$$

Analysis of the polarisation signs indicates the occurrence of CIDNP in the singlet radical pair ($R^{\bullet}\,{}^{\circ}Et$), but the authors do not regard electron transfer as the only possible reaction mechanism. Similar spectra have been observed in both solvents also for the reactions with $Et_2Pb(OAc)_2$ and Et_3PbOAc.

A wide variety of reactions involving organocopper compounds, including the reactions of RCu with organic halogeno-derivatives[98], have been investigated fairly vigorously in recent years. Some of these reactions have proved useful as regards syntheses; for example, the reactions of copper acetylides with a wide variety of halogeno-derivatives (acetylenic, vinyl, aromatic, etc.) are widely used for the synthesis of the corresponding hydrocarbons. In many instances thermally stable arylcopper compounds were introduced into the reaction with R′X. It is quite likely that some of these reactions proceed via a radical mechanism, but this problem has not been discussed in the literature. Furthermore, in many reactions, for example the reactions of arylcopper compounds with aromatic halides[99], a mixture of hydrocarbons is obtained, the formation of which can be readily explained by a radical mechanism. However, it is impossible to reach an unambiguous conclusion, because one cannot rule out the possibility that the formation of this mixture is associated with the occurrence of halogen–copper exchange processes, which has been demonstrated in many cases.

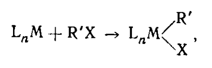
Somewhat more attention has been devoted (from the standpoint of the study of the mechanism) to the reactions of lithium (or magnesium) dialkyl- or diaryl-cuprates, which have higher thermal stabilities, with halogeno-derivatives[81,82]. The use of cuprates makes it possible to obtain high yields of the hydrocarbons RR′ in reactions with primary and even secondary RHal or ROTos (70–100%).

As already mentioned above, the reaction of lithium diphenyl- and dimethyl-cuprates with s-butyl bromide takes place preferentially (to the extent of 84–92%) with inversion of configuration, which shows that it proceeds via an S_N2 mechanism[81]. Similarly a 100% inversion of configuration is observed in the reaction of lithium diphenylcuprate with (+)-2-(s-butyl)toluene-*p*-sulphonate or ethanesulphonate in ether[100]. However, the reactions of cuprates with halogeno-derivatives of the vinyl series to form RR′ proceed with retention of geometrical configuration, which is clear evidence against an S_N2 mechanism. According to Whitesides et al.,[81] this mechanism is also relatively unsuitable for the explanation of the ease of reaction of lithium diphenylcuprate with aromatic halides (it is striking that the reaction may be regarded as a variant of the Ullmann reaction, for which both oxidation-reduction and heterolytic[101] mechanisms have been proposed). There is no doubt that, as in the reactions of organomagnesium and organolithium compounds, there may be a change of mechanism or a change in the contribution of the radical or heterolytic reaction pathway in the series of different cuprates, depending on their nature and that of R′X.

VIII. REACTIONS OF ORGANIC DERIVATIVES OF TRANSITION METALS WITH ALKYL HALIDES

The ability of certain transition metal complexes to undergo oxidative addition reactions (which includes the reactions with R′X) constitutes the basis of their catalytic activity in many processes, such as the homogeneous hydrogenation of unsaturated compounds, the oxidation of alkanes, etc., and also reactions involving the dissociation and reformation of carbon–carbon bonds.

The interaction of transition metal complexes with alkyl halides constitutes one of the most interesting methods for the formation of a carbon–metal σ-bond[102,103]. The reaction can proceed as oxidative addition, in which the state of oxidation of the metal and its coordination number change by two units (two-electron oxidation):



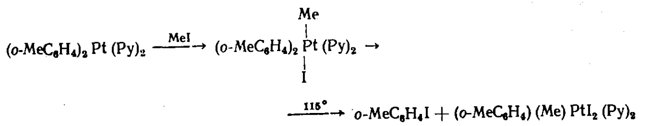
$$L_nM + R'X \rightarrow L_nM\begin{matrix}\diagup R' \\ \diagdown X\end{matrix},$$

where L is the ligand. In the presence of a fairly stable group to be eliminated from the alkylating agent (CH_3SbF_6, CH_3SO_3F), only one fragment R′ of the R′X molecule may add on[104,105] with formation of an alkylmetal cation, for example $[Pt(PPh_3)Me]^+$.

We shall naturally consider only reactions in which complexes of organic derivatives of metals are involved. The number of such reactions is small. The products of the addition of alkyl halides have been isolated for platinum(II) derivatives[106]; on heating, the complex decomposes with elimination of ethane:

$$[MePt(PEt_3)_2]I \overset{MeI}{\rightleftarrows} [Me_2PtI_2(PEt_3)_2] \xrightarrow{100^\circ} Me{-}Me + I_2Pt(PEt_3)_2.$$

It is postulated that the exchange of the *o*-tolyl group for methyl in the reaction[107]



$$(o\text{-MeC}_6\text{H}_4)_2\text{Pt(Py)}_2 \xrightarrow{\text{MeI}} (o\text{-MeC}_6\text{H}_4)_2\overset{\text{Me}}{\underset{\text{I}}{\text{Pt}}}(\text{Py})_2 \rightarrow$$

$$\xrightarrow{115°} o\text{-MeC}_6\text{H}_4\text{I} + (o\text{-MeC}_6\text{H}_4)(\text{Me})\text{PtI}_2(\text{Py})_2$$

proceeds via an intermediate of this kind.

The stereochemistry of the addition of MeI and CF_3I to platinum complexes, for example to *cis*-$Pt(Me_2)L_2$, has been studied[108]. The oxidative addition of methyl iodide to the triphenylphosphine complex of methylgold(I) proceeds via Me_2AuIL and the subsequent exchange of the alkyl halide with MeAuL gives a trimethylgold complex[109,110], which undergoes reductive elimination with formation of ethane:

$$\text{MeAuL} + \text{MeI} \underset{a}{\rightarrow} \text{Me}_2\text{AuIL} \xrightarrow[b]{\text{MeAuL}} \text{Me}_3\text{Au}^{\text{III}}\text{L};$$

$$\text{Me}_3\text{Au}^{\text{III}}\text{L} \underset{c}{\rightarrow} \text{Me—Me} + \text{MeAu}^{\text{I}}\text{L}.$$

Thus the complex MeAuL behaves as the catalyst in the dimerisation of alkyl groups[111]. A significant difference has been observed between the reactivities of the complexes in relation to oxidative addition (*a*) and alkyl exchange (*b*) processes as a function of the nature of the ligand. The complex Me_3AuPMe_3 is much more stable than Me_3AuPPh_3, so that it enters into a slow methyl–iodine exchange reaction with $IAu(PMe_3)$ or CH_3I without undergoing elimination.

It follows from the above mechanism that the oxidative addition reactions are assumed to have a polar mechanism. However, the possibility of a radical reaction pathway has been recently discussed in relation to an inorganic iridium(I) complex[112–114]. A free-radical chain mechanism is proposed for the process on the basis of the inhibiting effect of radical "traps" and the loss of configuration of the α-carbon centre in the reaction of $IrCl(CO)L_2$ with optically active ethyl α-bromopropionate[114].

There is another one-electron mechanism of the oxidation of transition metal complexes by alkyl halides:

$$2\text{L}_n\text{M} + \text{R}'\text{X} \rightarrow \text{L}_n\text{MR}' + \text{L}_n\text{MX}.$$

In this case the reaction undoubtedly proceeds via a free-radical mechanism:

$$\text{L}_n\text{M}^{\text{II}} + \text{R}'\text{X} \xrightarrow{\text{slow}} \text{L}_n\text{M}^{\text{III}}\text{X} + \text{R}'^{\cdot};$$

$$\text{R}'^{\cdot} + \text{L}_n\text{M}^{\text{II}} \xrightarrow{\text{fast}} \text{L}_n\text{M}^{\text{III}}\text{R}'.$$

The reactions involving the oxidation of iron(II) to iron(III) in porphyrins[115] and haemoglobin[116] by alkyl halides may serve as an example:

$$\rangle\text{Fe}^{\text{II}} + \text{R}'\text{X} \rightleftarrows \rangle\text{Fe}^{\text{II}}(\text{XR}') \rightarrow \rangle\text{Fe}^{\text{III}}\text{X} + \text{R}'^{\cdot}.$$

The fate of the radical depends on its nature; alkyl, benzyl, and propargyl radicals recombine to form R'_2. A further reduction of the radical with formation of alkanes is possible:

$$\text{R}'^{\cdot} + \rangle\text{Fe}^{\text{II}} + \text{H}^+ \rightarrow \rangle\text{Fe}^{\text{III}} + \text{R}'\text{H},$$

The alkanes are formed almost quantitatively when bromomalononitrile and diethyl bromomalonate are used as the alkyl halides[116].

The reactions of alkyl halides with cobalt[117,118] and chromium[119] complexes, leading to the formation of organic derivatives of these metals, have similar mechanisms. Generally speaking, these reactions involve the reduction of alkyl halides by metal salts (and not by organometallic compounds) and for this reason they are outside the scope of the review. We shall only mention that reactions of this kind include the alkylation of cobaloximes[120–122]:

$$2\text{Co}^{\text{II}}(\text{dmg})_2\text{L} + \text{R}'\text{X} \rightarrow \text{XCo}^{\text{III}}(\text{dmg})_2\text{L} + \text{R}'\text{Co}^{\text{III}}(\text{dmg})_2\text{L},$$

where dmg is dimethylglyoximate and L = Py, PPh_3, etc., and the reactions of R′X with vitamin B_{12s} [a cobalt(I) complex][123,124], which are biochemically important.

However, it is believed[122,123] that, in contrast to the reactions of $Co(CN)_5^{3-}$ (Halpern and Maher[117]) and cobaloximes[120], those of R′X with vitamin B_{12s} proceed as classical nucleophilic substitutions and do not involve electron transfer. This view is based on data for the influence of the nature of R′ on the course of the reaction. It is interesting to note that, according to the results of these investigations, vitamin B_{12s} is the most powerful nucleophile known (a supernucleophile[123]).

The stereochemical result of the reaction obtained in the alkylation of cobalt(I) cobaloximes by *cis*- and *trans*-1,4-dibromocyclohexanes, namely complete inversion at the carbon centre, also suggests that this process involves bimolecular nucleophilic S_N2 substitution[125].

IX. REACTIONS OF ORGANOBIMETALLIC COMPOUNDS† WITH ALKYL HALIDES

It is useful to examine briefly also data obtained for reactions of organobimetallic derivatives with alkyl halides, since in this case it is possible to note the same trend in the development of ideas concerning the reaction mechanism and the same difficulties in the determination of the mechanism which arise in the analysis of the results of studies on the reactions of RM with R′X. It is noteworthy that the reactions of $(R_{n-1}E_m)M$ with halogeno-derivatives constitute one of the methods for the formation of a C–transition metal σ bond.

Dessy et al.[126] investigated the reactivities of a series of compounds of the type $R_{n-1}E^-Bu_4N^+$ (where E are various Group IV and V metals and non-metals as well as transition metals, for example Fe, Cr, W, Mn, etc.) in relation to alkyl halides (MeI, EtBr, and iso-PrBr) in DME. The anions $R_{n-1}E^-$ were obtained via the electrochemical reduction of the corresponding derivatives, usually compounds of the type $(R_{n-1}E)_2$. Since no hydrocarbons of the type RH and R(–H) [or compounds of the type $(R_{n-1}E)_2$], which might have indicated a radical reaction mechanism, were detected in the products, the authors regarded the reaction as an S_N2 type process and the values of k_2 as a measure of the nucleophilic properties of the corresponding anions $R_{n-1}E^-$. However, the yields of bibenzyl (a "side" product) reached 47% in the reaction of trimethylsilylsodium with benzyl chloride, while the reactions of Me_3SiNa with butyl halides produced fairly large amounts of butane, the yield of which increased sharply on passing from the chloride to the bromide and to the iodide[127]. According to the authors[128], these results suggest the possibility of electron transfer with formation of radicals.

When triethylgermyl-lithium was allowed to react with chlorotriphenylmethane in benzene, the formation of the

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† Any compounds of the type $(R_{n-1}E^-)_mM^+$, where *n* is the valence of the element E, which may be both a metal or a non-metal, and *m* is the valence of the metal M, we have defined arbitrarily as organobimetallic derivatives.

triphenylmethyl radical was observed (13%), its yield reaching up to 33% after the addition of ether to the reaction mixture. Other reaction products were triethyl(triphenylmethyl)germane (63%) and hexaethyldigermane. The authors explained the results from the standpoint of the mechanism involving electron transfer from triethylgermyl-lithium to triphenylmethyl chloride[127,129]:

$$Et_3GeLi + Ph_3CCl \rightarrow \begin{bmatrix} Li^+ & {}^\cdot GeEt_3 \\ Cl^- & {}^\cdot CPh_3 \end{bmatrix} \rightarrow LiCl + Ph_3C^\cdot + Et_3Ge .$$

The same mechanism apparently obtained also in the reaction of bis(triethylgermyl)cadmium with triphenylmethyl chloride in toluene[127,129]. In this case the reaction is a multistage process. The first, exothermic stage involves the formation of the triphenylmethyl radical (according to ESR data). In the second stage, which is completed in several days at 20°C, metallic cadmium is formed. According to the authors, the exothermic stage involves electron transfer from $(Et_3Ge)_2Cd$ to Ph_3CCl:

$$(Et_3Ge)_2\,Cd + Ph_3CCl \rightarrow \begin{bmatrix} Et_3GeCd^+ & {}^\cdot GeEt_3 \\ Cl^- & {}^\cdot CPh_3 \end{bmatrix} \rightarrow Ph_3C^\cdot + Et_3GeCdCl + Et_3Ge^\cdot ,$$

$$2Et_3Ge^\cdot \rightarrow (Et_3Ge)_2 \quad (48\%);$$

$$Ph_3C^\cdot + Et_3Ge^\cdot \rightarrow Et_3GeCPh_3 \quad (28\%).$$

The fact that the organobimetallic derivatives enumerated readily reduce compounds such as naphthalene (Me_2SiNa), tetracyanoethylene, and *o*- and *p*-chloranils, i.e. typical electron acceptors, is regarded as evidence in support of the likelihood of the SET mechanism in these reactions[127-129]. Nor is a possibility of processes of the S_N2 type complicated by exchange processes ruled out. For example, the products found in the reaction of Et_3GeLi with triphenylmethyl chloride can be accounted for equally successfully by the following mechanism:

$$Et_3GeLi + Ph_3CCl \rightarrow Et_3GeCPh_3 + LiCl;$$

$$Et_4GeLi + Ph_3CCl \rightarrow Et_3GeCl + Ph_3CLi;$$

$$Et_3GeLi + Et_3GeCl \rightarrow (Et_3Ge)_2 + LiCl;$$

$$Ph_3CCl + Ph_3CLi \rightarrow 2Ph_3C^\cdot + LiCl.$$

However, for the analogous mercury derivative $(Et_3Ge)_2Hg$, the authors give preference to a heterolytic four-centre mechanism, assuming that unstable bis(triphenylmethyl)mercury is formed in the reaction as an intermediate:

$$(Et_3Ge)_2\,Hg + 2Ph_3CCl \rightarrow 2Et_3GeCl + \underset{\displaystyle 2Ph_3C^\cdot + Hg.}{\underset{\downarrow}{(Ph_3C)_2\,Hg}}$$

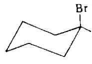
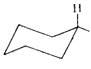
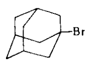
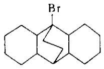
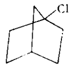
The reaction products are in fact mercury (93%), chlorotriethylgermane (68%), and hexaphenylethane‡ (91%). Hexaethyldigermane and triethyl(triphenylmethyl)germane could not be detected in the reaction mixture[129]. The same four-centre mechanism has been proposed also for the reaction of $(Et_3Ge)_2Hg$ with simple alkyl or aryl halides[127-131] and for the reaction of $(Me_3Si)_2Hg$ with aryl halides[133]. The authors of the last investigation believe that virtually all the products can be accounted by an S_Ni mechanism; if the radical reaction pathway does occur, its contribution is very small. The reaction of triphenylstannylsodium with 1-bromoadamantane in liquid ammonia probably proceeds via a radical mechanism[134].

A mechanism including the SET stage has been proposed for the reaction of sodio- and potassio-dibutylboron with alkyl halides (MeI, n-HepI, $PhCH_2Br$, and $PhCOCH_2Br$). The formation of a mixture of RH, R_2, and Bu_3B was observed in all cases; the yield of the product of the Wurtz reaction proper was vanishingly small under these conditions (< 1%).[135]

X. STEREOCHEMISTRY OF REACTIONS OF ORGANOBIMETALLIC COMPOUNDS WITH ALKYL HALIDES

There have been several studies on the stereochemistry of reactions of organobimetallic derivatives of Group IV elements with alkyl halides (Table 6).

Table 6. Stereochemical data obtained for the reactions of organibimetallic compounds with various R'X.

$R_{n-1}E^-M^+$	R'X	Solvent	Stereochemical result	Refs.
Ph_3SiLi	s-C_4H_9Br	THF	51% inversion	136
Ph_3GeNa	»	NH_3(liq.)	67% inversion	»
Ph_3SnNa	s-C_4H_9Cl	DME	90% inversion	»
Ph_3SnNa	s-C_4H_9Br	DME	88% inversion	»
»	s-C_4H_9I	DME	71% inversion	»
Ph_3PbNa	s-C_4H_9Br	NH_3(liq.)	67.5% inversion	»
$(CH_3)_3SnNa$	*syn*-7-bromonorborn-2-ene	NH_3(liq.)	inversion	137
»	*anti*-7-bromonorborn-2-ene	»	*syn–anti* + tricycl. mixture	»
$(CH_3)_3SnLi$		THF	retention	139
»		»	inversion	»
»		»	retention	»
»		»	”	»
»		»	”	»
$(CH_3)_3SnLi$	*syn*-7-bromonorbornene	THF	84% inversion	140
»	»	DME	97% inversion	»
»	»	THF–TG	”	»
$(CH_3)_3SnNa$	»	THF	10% inversion (90% retention)	»
»	»	DME	81% inversion	»
»	»	THF–TG	91% inversion	»
$(CH_3)_3SnK$	»	THF	47% inversion	»
»	»	DME	18% inversion	»
»	»	THF–TG	96% inversion	»
$CH_3)_3Sn$(Li, Na, K)	*anti*-7-bromonorbornene	THF DME THF–TG	79–99% retention	»
$(CH_3)_3SnLi$	1-bromomethyl-2,2-diphenylcyclopropane	THF	retention	138

Jensen and Davis[136] observed the preferential inversion of configuration in the reactions of Ph_3EM (E = Si, Ge, Sn, or Pb) with optically active s-butyl halides (Hal = Cl, Pr, or I), the extent of inversion of configuration increasing from the iodide to the chloride. In conformity with the study of Dessy et al.,[126] the authors treat their results as a consequence of an S_N2 process. However, as already pointed out in the discussion of the stereochemistry of the Wurtz reaction, the S_N2 mechanism explains only the inversion of configuration; in order to

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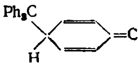
‡ The triphenylmethyl dimer[132] having the structure



is probably meant.

account for the observed partial racemisation (Table 6), one must invoke another mechanism or the parallel occurrence of an exchange process and the loss of configuration in the organometallic compound RM formed. An inversion of configuration has also been observed in the reaction of trimethylstannylsodium with *syn*-7-bromonorborn-2-ene in liquid ammonia, but the analogous reaction with the *anti*-isomer led to the formation of a mixture of *syn*- and *anti*-isomers[127]. The reaction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane with Me_3SnLi takes place with retention of configuration[138].

The problem of the mechanisms of the reactions of organobimetallic compounds with **R'X** has been examined by Traylor et al.,[139] who investigated the stereochemistry of the reactions of trimethylstannyl-lithium with a series of halogeno-derivatives of cyclohexane, bi- and tri-cyclic compounds, and 4-t-butylcyclohexyltoluene-*p*-sulphonate (Table 6). The authors believe that the inversion of configuration is always a consequence of a reaction of the S_N2 type at the carbon atom. On the other hand, the observed retention of configuration can be accounted for on the basis of two mechanisms according to their view.

1. The metal–halogen exchange process, which the authors regard as an S_N2 reaction involving the halogen atom followed by a rapid Wurtz reaction:

$$R'Br + R_3SnLi \xrightarrow{\text{slow}} R'Li + R_3SnBr; \text{ (retention of configuration).}$$

$$R_3SnBr + R'Li \xrightarrow{\text{fast o}} R_3SnR' + LiBr.$$

The authors suggest that the first stage proceeds with retention of configuration and the second stage probably also takes place with retention of configuration as a process of the S_E2 type involving the carbon atom. Furthermore, the RLi formed in the reaction are not racemised, probably owing to the structure of the R group.

2. A mechanism involving the SET stage:

$$R'Br + R_3Sn^- \rightarrow [R'^{\cdot}Br^- \ {}^{\cdot}SnR_3] \rightarrow R'SnR_3 + \text{olefin.}$$

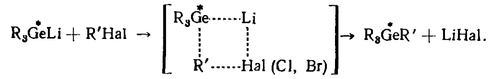
Both mechanisms also explain the formation of distannane observed in the reaction, but the authors give preference to the former on the grounds that the geometrical configuration is retained in the reaction with *cis*-4-t-butylcyclohexyl bromide, while under conditions allowing rotation in the radical-ion pair the R_3Sn^- group should have occupied the more stable equatorial position.

To a significant degree, the stereochemistry of processes of this kind can depend on the nature of the solvent and the atom of the metal M. The results obtained by Kuivila et al. for the reactions of the *syn*- and *anti*-isomers of 7-bromonorbornenes with Me_3SnM in a series of ethereal solvents[140] are presented below.

		Retention of configuration, %		
Isomer	M	THF	DME	THF–TG
syn-	Li	16	3	,3
	Na	90	18	9
	K	3	92	4
anti-	Li	96	98	96
	Na	85	93	99
	K	79	92	96

The authors regard the results obtained as confirmation of the view that the "freer" ion pairs react preferentially with inversion of configuration. Indeed, in the case of the *syn*-isomer the highest percentage inversion is observed in the THF-tetraglyme (TG mixture) and for the lithium derivatives, which are most highly solvated, in all the solvents. A particularly marked solvent effect has been observed in the reaction with Me_3SnNa, where the stereochemical result varies from 70% retention in THF to 91% inversion in the THF–TG mixture. However, incomprehensible results have been obtained for the *anti*-isomer—the reaction proceeds in all solvents with almost complete retention of configuration. The reactions of 1- and 2-bromoadamantanes with Me_3SnM also involve a complete retention of configuration[140]. Analysis of the possible reaction mechanisms led the authors to the conclusion that the retention of configuration can be most simply explained by a four-centre transition state, although the alternative two-stage process and the mechanism including an SET stage (Traylor's mechanisms 1 and 2[139]) are not ruled out. We may note that, in the Wurtz reaction between RM and optically active alkyl halides, the retention of configuration in the product **RR'** has not been observed with the exception of the reactions of **RM** with vinyl halides, which take place with retention of geometrical configuration.

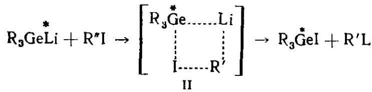
Finally, Eaborn and coworkers[141,142] studied the stereochemistry of the reactions of optically active ethylphenyl(α-naphthyl)germyl-lithium with a series of alkyl halides in ether and showed that the stereochemical result depends significantly on the nature of the halogen. Thus the reactions with chlorides and bromides took place predominantly with retention of the configuration at the germanium atom, while inversion of configuration was observed in the reactions with iodides. The configuration was retained also in the reaction with benzyl bromide. The authors explained the retention of configuration in this reaction by a four-centre transition state (I):



$$R_3\overset{*}{Ge}Li + R'Hal \rightarrow \left[\begin{array}{ccc} R_3\overset{*}{Ge} & \cdots & Li \\ \vdots & & \vdots \\ R' & \cdots & Hal \text{ (Cl, Br)} \end{array}\right] \rightarrow R_3\overset{*}{Ge}R' + LiHal.$$

(I)

On the other hand, they believe that in reactions with iodides the exchange process (II) takes place initially and is followed by the Wurtz reaction between R_3GeI and **R'Li**, which results in inversion of configuration, as shown by the same investigators[143]:



$$R_3\overset{*}{Ge}Li + R''I \rightarrow \left[\begin{array}{ccc} R_3\overset{*}{Ge} & \cdots & Li \\ \vdots & & \vdots \\ I & \cdots & R' \end{array}\right] \rightarrow R_3\overset{*}{Ge}I + R'Li;$$

II

$$R_3\overset{*}{Ge}I + R'Li \xrightarrow{\text{inversion}} R_3GeR' + LiI.$$

Thus analysis of the stereochemical data for the reactions of organobimetallic derivatives with **R'X** shows that the results cannot be accounted for by a single mechanism (as already stated, a similar situation was observed also for the reactions of **RM** with **R'X**).

XI. THE INTERACTION OF ORGANOMETALLIC COMPOUNDS WITH 'ONIUM SALTS

A radical mechanism has been proposed for the reactions of iodonium salts with Grignard reagents by Gragerov and coworkers[144] on the basis of the detection of triphenylmethyl radicals in the reactions of diphenyliodonium salts ($X = BF_4$, Cl, or I) with triphenylmethylmagnesium chloride and the detection of methane and ethane (5%) in the reaction of $Ph_2I^+BF_4^-$ with methylmagnesium iodide:

$$Ph_2I^+X^- + RMgX' \rightarrow Ph_2I^{\cdot} + R^{\cdot} + MgXX'.$$

However, the problem of whether the radical pathway is unique or whether it represents a side reaction, which becomes dominant for $R = Ph_3C$, remains unsolved.

A similar mechanism has been suggested also for reactions of t-butyl- and benzyl-magnesium chlorides with *p*-chlorophenyldiazonium fluoroborate in THF.[145] PhCl (40%), *p*-$ClC_6H_4N = NCMe_3$ (15,6%), isobutane (18%), isobutene (14%), and tetramethylbutane (77%) were detected in the former reaction. Furthermore, the polarisation of the vinyl protons of isobutene and of the methyl protons of isobutane was observed. The formation of chlorobenzene, toluene, and bibenzyl was noted in the reaction with benzylmagnesium chloride; chlorobenzene proved to be polarised. A study was also made of the interaction of diphenyliodonium bromide with methyl-, ethyl-, and phenyl-magnesium iodides and phenyl-lithium, toluene (59%), ethylbenzene (37%), and biphenyl (33 and 64% respectively) being observed. The authors were not particularly concerned with the study of the reaction mechanism, but they believe that the reaction is a process of the S_N2 type.[146]

The reaction of diphenyliodonium fluoroborate with α-bromomercuriphenylethyl acetate, which leads to the formation of a mixture of ethyl esters of phenylacetic, diphenylacetic, and 1,2-diphenylsuccinic acids, can only be treated from the standpoint of the SET mechanism[147]:

$$Ph_2IBF_4 + PhCH(HgBr)CO_2Et \rightarrow PhCH_2CO_2Et + Ph_2CHCO_2Et + (PhCHCO_2Et)_2.$$

Within the framework of the SET mechanism, an attempt could probably be made to treat the interaction of organolithium compounds with the sulphonium salts $Ph_3S^+BF_4^-$.[148-150] However, the experiments carried out using phenyl-lithium labelled with ^{14}C showed that, for the 1 : 1 reactant ratio, the isotopic label is distributed in equal amounts between the reaction products Ph_2 and Ph_2S, which agrees with the mechanism involving their formation from the intermediate sulphurane Ph_3Ph^+S, but can also be accounted for within the framework of the SET mechanism or on the assumption of the intermediate formation of dehydrobenzene[149]. Furthermore, the existence in solution at a low temperature (−78°C) of tetrakis(pentafluorophenyl)sulphurane, which decomposes on raising the temperature (−20° and 0°C) with formation of the corresponding fluorinated analogues of biphenyl and diphenyl sulphide, has been demonstrated. On the other hand, the addition of styrene or norbornene has no influence on the course of the reaction[150].

It is apparently of interest to investigate the reactions of organomagnesium compounds with sulphenyl chloride[151,152] for which an electron transfer stage may be postulated in certain cases, bearing in mind that sulphenyl halides are reduced much more readily than alkyl or aryl halides[153,154]:

$$ArSCl\ (AlkSCl) + Ar'MgX \rightarrow ArSAr'\ (AlkSAr') + MgXCl.$$

Unfortunately, a complete analysis of the products was not carried out in the above investigations[151,152] and only the yields of the corresponding sulphides are indicated (55–70%), which does not allow one to infer that radical stages occur in the reaction.

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Polymerisation of Acetylenes. The Structure and Electrophysical Properties of Polyvinylenes

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The literature data on the radical and ionic linear polymerisation of mainly mono- and di-substituted acetylenes with a single carbon–carbon triple bond are considered and the known mechanisms of the acetylene polymerisation processes are discussed. Much attention is devoted to the copolymerisation of acetylenes with monomers of different types. The results of studies on molecular, supermolecular, and electronic structures of polyvinylenes are compared with their electrophysical properties. The bibliography includes 475 references.

CONTENTS

I. INTRODUCTION

There has been a considerable growth of interest in recent years in the study of the polymerisation reactions of acetylenic compounds which make it possible to synthesise linear and cyclic compounds with a wide variety of structures. Different aspects of the problem have been described in a number of reviews and monographs[1–25].

The aim of the present review is to consider the latest advances in the synthesis of linear polymers based on mono- and di-substituted acetylenic monomers with a single C≡C bond. A review of studies on the polymerisation of diacetylenes was published previously[26]. To facilitate the description and in view of the fact that the polymerisation mechanism has not been established in many cases, a systematic account is given of the available data in accordance with the initiator or catalysts employed in the synthesis of the polymers.

The unusual features of the reactivities of alkynes are determined largely by the high electron density in the triple bond, the cylindrical symmetry of the electron distribution relative to the molecular axis, and the weak polarisability of π electrons, which hinders electrophilic attack and facilitates nucleophilic attack on the triple bond[27]. Because of the above characteristics, alkynes readily form π complexes[15] and metal acetylides[15,27]. Thus one may expect the polymerisation of alkynes to occur most readily under the influence of anionic and complex catalysts based on transition metal compounds. On the other hand, one should bear in mind that the ease of elimination of the acetylenic proton promotes chain termination and transfer, while strong bases induce the acetylene–allene rearrangement[27,28].

The relative weakness of the multiple carbon–carbon bonds compared with a single bond is the driving force of the polymerisation of unsaturated compounds. The polymerisation usually leads to a decrease of entropy and sometimes also the enthalpy of the system[29]. In the polymerisation of acetylenes, the change in the enthalpy of the system is a consequence of the replacement of the triple bonds by the more stable double bonds and the stabilisation of the resulting polyconjugated system[30]. The conjugation energy per unit in the polyvinylene (polyacetylene) chain is a function of the number of units and increases continuously up to the limiting value of 0.55 β, where β is the resonance integral or 10 kcal. The overall enthalpy of polymerisation of acetylene to give a polymer stabilised by conjugation should be 46 kcal mole^{-1}.[31] According to an estimate[30], the negative entropy of polymerisation of acetylene is −34.5 e.u.

II. RADICAL POLYMERISATION

1. Thermal Initiation

The reactions of phenylacetylene (PA) have been investigated in greatest detail. From approximately 120°C, amorphous, soluble, and coloured linear polyene is formed from PA (together with 1–25% of triphenylbenzenes)[32–41]. The molecular weight of the polymer $\bar{M}_n$ depends little on the polymerisation conditions[33,42]. An approximately twofold increase of the number-average degree of polymerisation (up to $\bar{P}_n = 26$) has been observed in the polymerisation of PA in the presence of polyphenylvinylene (poly PA) obtained beforehand[43,44]. The polymerisation of PA under pressure (80–200°C, 1000–6000 atm) proceeds at a much higher rate than under normal pressure, but the degree of polymerisation hardly changes[45,46].

The thermal polymerisation of PA can be explained satisfactorily in terms of a bimolecular initiation mechanism[36,37]. It is believed that there is a possibility of the formation under these conditions of the two most stable biradicals: triplet (*trans*-1,4) and singlet (*cis*-1,3). The first leads to mainly the chain propagation of the linear polymer and the second the formation of triphenylbenzenes. The polymerisation reaction is of second or higher order with respect to the monomer (2 in nonane and cyclohexane[37,47], 2.20 in xylene[36], and 2.32 in benzene[48]). The deviation towards the trimolecular reaction is probably associated with the formation of considerable amounts of cyclic trimers on bimolecular initiation and first-order termination. The rate of polymerisation in bulk is proportional to the concentration of PA, possibly in consequence of the gel effect. The activation energies for the polymerisation process E_a are respectively 26.8 and 33.67 kcal mole^{-1} in bulk[36] and in solution [37,47]. The termination of the growing macroradical probably occurs via degradative chain transfer to the monomer. Chain termination in the course of intramolecular cyclisation has also been postulated[47].

Pyridylacetylenes[49] and 5-ethynyl-2-methylpyridine polymerise similarly to PA.[36] The polymerisation of 5-ethynyl-2-methylpyridine[36] (125–175°C, solution in *p*-xylene) is of second order with respect to the monomer (E_a = 20.4 kcal mole^{-1}).

A soluble polymer with $\overline{M}_n$ = 950 has been obtained from *p*-dimethylaminophenylacetylene (150°C, 24 h) in 66.5% yield; *p*-nitrophenylacetylene (200°C, 4 h) gives rise to a partly soluble polymer in 97% yield and *o*-nitrophenylacetylene polymerises explosively at 150°C.[50] The polymerisation of *o*- and *p*-nitrophenylacetylenes takes place under the influence of cold plasma[51].

Acetylenic derivatives of condensed aromatic hydrocarbons (ethynylnaphthalene[52], 9-ethynylanthracene[53], 9-ethynyl phenanthrene[54], 5-ethynylacenaphthene[55], the 1,2-dihalogenoacenaphthylene dehydrohalogenation product[56], and *N*-ethynylcarbazole[57]) polymerise comparatively readily at 100–220°C (9-ethynylanthracene even at room temperature).

Under normal pressure, propargyl alcohol does not polymerise up to 200°C, but at an elevated pressure (6000 atm) it is converted into a polyene in 11% yield at a temperature as low as 120°C.[58] With increase of temperature, the yield of the insoluble product formed as a result of cross-linking via intermolecular elimination of water also rises. Intramolecular and intermolecular cross-linking processes have also been observed in the polymerisation of propiolic acid under pressure[59–61]. The polymerisation of the ethers formed by the interaction of propargyl alcohol with phenol and its *m*-methyl- and *p*-*t*-butyl derivatives takes place with an induction period, which diminishes with increase of reaction temperature (45 h at 160°C, 1 h at 250°C) and leads to low-molecular-weight products[62]. *N*-Propargylmorpholine also polymerises with an induction period[63]. With increase of the length of the alkyl group, the yield of poly-(*N*-alkyl-*N*-propargylamines) (polymerisation in bulk at 200–250°C, $\overline{P}_n$ = 5–9) diminishes, probably owing to a steric effect and a change in the polarisability of the triple bond[64].

A substituted polyene with $\overline{M}_n$ = 2700 is formed from ethynyltriphenylgermane at 180°C.[65]

Phenoxyacetylene polymerises spontaneously even at room temperature. The resulting polyene chains are cross-linked via a Diels-Alder reaction to hydroaromatic derivatives, which are aromatised by the elimination of phenol[66]. E_a 23.1 kcal mole^{-1} for phenoxyacetylene and free-radical initiators do not influence its spontaneous polymerisation[67,68]. Phenylthioacetylene is less reactive and *p*-nitrophenoxyacetylene is much more reactive in polymerisation than phenoxyacetylene[67,68]. The structures of the polymerisation products of 2-methoxy-1-phenylacetylene[66] and ethoxyacetylene[66,69] have not been determined.

In contrast to arylacetylenes, alkylacetylenes polymerise under more severe conditions[46,70,71]. Cyclohexylacetylene oligomers with $\overline{M}_n$ = 400–500 (E_a = 32.7 kcal mole^{-1}) have been obtained at a temperature in excess of 230°C.[70] It has been suggested[72] that the thermal polymerisation of alkylacetylenes occurs only in the presence of an admixture of allenes, which initiate the process. But-2-yne gives rise (250°C, 23.5 kbar) to an insoluble resin containing non-conjugated double bonds according to infrared spectroscopic data, which may indicate the formation of a ladder structure[73].

Disubstituted acetylenes polymerise at higher temperatures than the monosubstituted derivatives. For example, tolane polymerises at 300–400°C [74,75] and $\overline{M}_n$ for the polymers increases from 850 to 1200 when the temperature rises from 300 to 400°C. A bimolecular initiation mechanism has been suggested.

The dimethyl and diethyl esters of acetylenedicarboxylic acid polymerise at temperatures in excess of 200° and 300°C respectively[76]. The polymerisation of β-iodophenylacetylene is extremely complex and is accompanied by the evolution of iodine[77,78].

When diiodo and dichloro-maleic anhydrides or diiodo-*N*-phenylmaleimide were dehalogenated, the products were polymers resulting from the dissociation of the triple bond in the hypothetical anhydride of acetylenedicarboxylic acid or its analogue[79].

2. Polymerisation in the Presence of Initiators

The initiated radical polymerisation of acetylenes has no advantages over the purely thermal process. This is indicated by the extremely limited selection of initiators, a significant contribution of thermal processes in many instances, hindering the study of the reaction kinetics, the low conversion of the monomer, the low molecular weight of the resulting polymer, and the contamination of the polymer by the initiator decomposition products.

The initiators employed were benzoyl peroxide (BP),[45,80–111] lauroyl peroxide[88,112], t-butyl peroxide[45,58,107–110], azobisisobutyronitrile (ABIN),[45,89–94,96–98,100–102,104–106,111–118], triisobutylboron[45], triisopropylboron[43,44,112,119–122], and triethylboron[123]. The benzoyl peroxide initiator does not undergo simple thermal dissociation (60–80°C) and is involved in a chain reaction with monomer molecules. It has been shown for PA [84,124] that two radicals are formed under these conditions, one of which propagates the polymerisation and the other abstracts hydrogen from the monomer with formation of benzoic acid and an inactive radical; this is confirmed by the kinetics of the decomposition of benzoyl peroxide in PA, deuterophenylacetylene, and methylphenylacetylene. ABIN does not undergo chain decomposition in the presence of PA.[111] The formation of isopropyl hydroperoxide on polymerisation of PA in the presence of triisopropylboron and oxygen appears to indicate a radical process mechanism[119]. In the absence of oxygen, PA does not polymerise under the influence of triethylboron.

The rate of polymerisation of PA is proportional to the concentration of the monomer and the initiator (benzoyl peroxide), one polymer molecule being formed on decomposition of one peroxide molecule[84,85]. With increase of temperature (60–130°C), the rate of polymerisation rises appreciably and $\overline{M}_n$ varies in the range 600–1500.[85] It is suggested[125] that E_a for the radical-initiated polymerisation of acetylenes should equal the decomposition energy of the initiator (about 21 kcal mole^{-1} in the polymerisation of PA).

Benzoquinone inhibits the polymerisation of PA under the influence of benzoyl peroxide, which is probably associated with the suppression of the above initiation reaction by benzoquinone[84]. On the other hand, benzoquinone apparently does not inhibit the growing radical, since the radiation-induced and ABIN-initiated polymerisation of PA proceeds also in the presence of benzoquinone[111]. The rate of polymerisation of PA in the presence of triisopropylboron is of first order with respect to the monomer. The initiator concentration hardly affects the yield of the polymer, which is strongly influenced by the reaction temperature. The break in the lg *k*–1/*T* curve, where *k* is the effective polymerisation rate constant, corresponds to activation energies of 78 and 29 kcal mole^{-1}, which has not been explained[43,119,120,122].

The rate of polymerisation of ethynylferrocene in the presence of benzoyl peroxide, lauroyl peroxide, and triisopropylboron in bulk at 140–200°C is proportional to the monomer concentration and $E_a \simeq 10$ kcal mole^{-1}. Up to 190°C, the concentration of benzoyl peroxide (0.2–1.6%) does not affect the yield of the polymer. The conversion passes through a maximum at 190°C and for soluble fractions $\bar{P}_n = 4$–7.[86,87,112] In contrast to benzoyl peroxide[126], t-butyl peroxide did not oxidise ethynylferrocene and did not cause the degradation of the polymer under the conditions employed (160–180°C; molar ratio initiator : monomer = 0.25 : 1).[107–110] It is suggested that the radical formed on decomposition of the initiator abstracts from the monomer the mobile acetylenic hydrogen. The monomeric radical is stabilised in the form of the dimer (diferrocenylbutadiyne) which polymerises and is methylated owing to the decomposition of some of the butoxy-radicals.

It has been shown for 1-chloro-1′-ethynylferrocene[88] that the chlorine atom located in a heteroannular position relative to the ethynyl group greatly reduces the capacity of the monomer for polymerisation. A linear polyene structure, which may be crossed-linked via chlorocyclopentadienyl rings, has been proposed for the polymer.

Propiolaldehyde polymerises via the mechanism[114]

$$n\mathrm{HC{\equiv}C{-}CHO} \xrightarrow[1.9\%]{\mathrm{AIBN}\ 60°,\ 19\mathrm{h}} -[-\mathrm{HC{=}C(CHO){-}}]_n- \quad .$$

Propargyl acrylate[89–93], methacrylate[90–92], crotonate[92], itaconate[91], and acetate[94] were polymerised in bulk and in solution under the influence of ABIN and benzoyl peroxide at 60–80°C. For the first three monomers, the rate of reaction is proportional to the initiator concentration raised to a power of 0.7 and 0.8 in the presence of benzoyl peroxide and ABIN respectively and to the monomer concentration raised to a power of 1.6 in both cases; $E_a =$ 16–21 kcal mole^{-1}. For conversions up to 20–30%, polymerisation takes place via the dissociation of the double bonds, after which the triple bonds also react with the consequent formation of three-dimensional systems.

Vinylacetylene polymerises in the gaseous state at 250–400°C in the presence of small amounts of oxygen[127,128]. The rate of reaction is proportional to the monomer concentration raised to the power 1.94; $E_a = 25.3$ kcal mole^{-1}. The polymerisation of vinylacetylene in the presence of benzoyl peroxide takes place in a more complex manner[80,81]. Oligomers (ABIN; $\bar{P}_n = 4$–15) of divinylacetylene were obtained; oxygen accelerates the process and oxidises the polymer[116,117].

Numerous studies have been made on the polymerisation of ethynyldimethylvinylmethanol and its esters and ethers. Polycyclobutene[1,5,129] or polycyclopentene[11,94–104,118] structures, resulting from cyclopolymerisation involving the double and triple bonds, were proposed for the resulting polymers. Other investigators believe that the polymerisation proceeds only with participation of the double bonds[105,106] or with participation of the double bonds in the isopropenylacetylene series and with formation of cyclopentene rings in the vinylacetylene series[130].

A soluble polytolane was obtained in low yield under the influence of a shock wave. It is suggested that this involves a special type of polymerisation—"polymerisation in the shock wave"[131].

3. Radiation-Induced Initiation and Photoinitiation

The radiation-induced polymerisation of PA has been investigated in greatest detail. It has been carried out over a wide range of temperatures (between −196° and 100°C) in bulk and in solution under the influence of initiating radiation at different dose rates (36–10^6 r min^{-1}) and over a wide range of doses (10^6–10^8 r). Radiation polyPA—a yellow-orange amorphous product, soluble in many organic solvents, with a softening temperature of about 200°C, and with $\bar{M}_n = 1200$—was obtained in a yield of 10–12%. The radiation-chemical yield of the polymer G (the number of polymerising monomer molecules per 100 eV) is 8–9 [124,125,132–134] for irradiation with accelerated electrons (1.6 MeV) and 8–13,[135,136], 13–30,[137] and 30–40 [138] for irradiation with cobalt-60 γ-rays.

The mechanism of the radiation-induced polymerisation of PA is determined largely by the process temperature. Gol'danskii and coworkers[124,125,132–134] suggested that PA polymerises via a radical mechanism in both liquid and solid phases. Japanese investigators[118] believe that ionic polymerisation takes place at low temperatures; the possibility of an "electronic" mechanism is not ruled out either[139].

The rate of polymerisation of PA is proportional to the rate of initiation, i.e. to the dose rate. The same dependence has been observed in the polymerisation of propiolic acid and its salts[60,140–143], propargyl alcohol[138,144–146], and propargyl bromide[138,148,149]. This indicates the absence of bimolecular termination of the macroradicals when a radical process mechanism is postulated, which can be accounted for by the loss of activity by the growing radical owing to the increase of the degree of delocalisation of the unpaired electron. Instead of separating the chain propagation and termination reactions, it was suggested that a single polymer chain "decay" process be considered[125]. Subsequently this hypothesis was refined; the importance of the mobile acetylenic hydrogen, terminating both the material and the kinetic chain in consequence of the formation of an inactive radical, was noted[134]. Another important characteristic of the radiation-induced polymerisation of PA is the low value of E_a (~700 cal mole^{-1}) and hence the virtual independence of the rate of the process of temperature, which is characteristic of the ionic polymerisation of olefins.

In the presence of oxygen, the yield of polyPA increases by a factor of 1.2–2.[120,132,133] The polymerisation is not inhibited by radical process inhibitors (benzoquinone), possibly owing to the fact that the interaction of the inhibitor with radicals at a high steady-state concentration, i.e. with delocalised macroradicals which have lost their activity, is the most likely process. When PA was polymerised in solution in nonane or ethyl acetate, an appreciable deviation from additivity was noted, which indicates an effective transfer of the irradiation energy absorbed by the solvent to the monomer[124,132]. A specific feature of the polymerisation of PA in the liquid phase is the independence of the yield of the polymer of dose rate (for a given dose)[125], which is characteristic of the radiation-induced solid-phase polymerisation of vinyl monomers. For polyPA's, $\bar{M}_n$ is almost independent of the polymerisation temperature, the rate of initiation, the form of the initiating radiation, the monomer concentration, and the phase state. The use of radiation-induced initiation made it possible to graft PA to fibreglass[149].

The radiation-induced polymerisation of alkylacetylenes (propyne, hex-1-yne, oct-1-yne, and cyclohexylacetylene) proceeds similarly[124,132–135]. The rate of reaction is proportional to the dose rate: $E_a \simeq 1$ kcal mole^{-1} and $\bar{P}_n = 10-13$. A white insoluble thermostable polymer, resistant to the action of concentrated acids and alkalis, was obtained in the polymerisation of perfluorobut-2-yne under the influence of cobalt-60 γ-radiation[150] or electrons with energies in the range 0.5–4 MeV.[151]

Radiation-induced initiation has many advantages compared with thermal initiation and photoinitiation in the case of propiolic acid and its salts (fewer side reactions, the radiolysis of the monomer does not exceed 1–1.5%).[60, 140–143] For a dose of 124 Mr about 30% of amorphous polymeric acid with $\bar{M}_n = 3000$ and $G = 35-40$ is formed. According to infrared spectroscopic data, the *trans*-transoid configuration of the polyene chain arises in solid-phase polymerisation and the *trans*-cisoid configuration arises in liquid-phase polymerisation. At −196°C polymerisation does not occur and, on increase of temperature to between −120° and −100°C, postpolymerisation is observed. The reactivity of propiolate salts is determined by the stability of the crystal lattice (the radius and valence of the cation).

In the study of the radiation-induced polymerisation of 59 different acetylenic monomers, polymeric products were obtained only from acetylenedicarboxylic acid and neopentylene dipropiolate[13].

An ethynylferrocene polymer with $\bar{M}_n = 1000-3000$ was obtained in a yield of about 4% (γ-irradiation, 270 Mrad).[152]

The photopolymerisation of PA,[153] methyl 4,4-dimethylpent-2-ynoate[154], tolane[155], and propargyl bromide[148] has been investigated very inadequately.

III. IONIC POLYMERISATION

1. Cationic Polymerisation

An unsuccessful attempt to polymerise vinylacetylene and 3-ethylvinylacetylene in the presence of BF_3 and $AlCl_3$ was reported in 1959.[156] However, later it proved possible to polymerise both vinylacetylenes $RC{\equiv}CCH{=}CH_2$†, where R=R, Et, $Me_2(OMe)C$, or $CH_2{=}OMe$ [BF_3,[157,158] $BF_3.OEt_2$,[159–161] CCl_3COOH,[158,161] CF_3COOH,[158] H_2SO_4,[159] and $SnCl_4$ [159,160]] as well as other acetylenic monomers: pent-1-yne [$SnCl_4$ [162]], phenylacetylene [BF_3,[163] $BF_3.OEt_2$,[39,164] CF_3COOH,[39,164] CCl_3COOH,[155,166] $SnCl_4$,[162] and AlX_3 with X_3 = Cl_3, $EtCl_2$, Et_2Cl, or Et_3 [167]], 9-ethynylanthracene [$TiCl_4$ [53]], *p*-methoxyphenylacetylene [$BF_3.OEt_2$ and CF_3COOH [38,164]], $Me_2NC{\equiv}CC(O)R$ with R = H or Me [$TiCl_4$, $SnCl_4$, H_2SO_4, HBF_4, $BF_3.OEt_2$, $Et_3N.HBr$, or CF_3COOH [168]], and $ROC{\equiv}CH$ with R = Me, or iso-Bu [Friedel-Crafts catalysts[169]].

In the reaction of acetylene containing a powerful electron-accepting substituent ($NC-C{\equiv}CH$) using $TiCl_4$, $Co(Acac)_3$ (Acac = acetylacetone), and $AlEt_3$ as catalysts, a polymer is formed only in the last case, its yield being much lower than in the Ziegler polymerisation[169]. PA reacts with $SnCl_4$ to form a stable complex; polymerisation takes place after the addition of hydrochloric acid, which behaves as a cocatalyst[162].

The main product formed in the reaction of PA in the presence of CCl_3COOH (in benzene at 30–55°C) is 1-phenylvinyl trichloroacetate formed as a result of the addition of CCl_3COOH to the C≡C bond of the monomer. Acetophenone and about 3% of a low-molecular-weight linear polymer with a conjugated system were also detected.

It has been suggested[165] that the catalyst participates in the reaction in a dimeric form $(HA)_2$ and forms with the monomer an intermediate of the solvated ion pair type (A = anion):

$$HC{\equiv}CPh + 2\,(HA)_2 \rightleftarrows (CH_2{=}\overset{+}{C}Ph\bar{A}HA)\cdot(HA)_2.$$

This ion pair leads to the formation of low-molecular-weight products and initiates the polymerisation of PA:

$$(CH_2{=}\overset{+}{C}Ph\bar{A}HA)\cdot(HA)_2 + HC{\equiv}CFh \rightarrow (CH_2{=}CPhCH{=}\overset{+}{C}Ph\bar{A}HA)\cdot(HA)_2;$$
$$(CH_2{=}CPh-[-CH{=}CPh-]_n-CH{=}\overset{+}{C}Ph\bar{A}HA)\cdot(HA)_2 \rightarrow$$
$$\rightarrow (CH_2{=}CPh-[-CH{=}CPh]_{n+1}A + (HA)_2 + HA.$$

The reaction of PA with CCl_3COOH in nitroethane solution is of first order with respect to the monomer and of third order with respect to the catalyst, about 15% of a linear polymer with $\bar{P}_n = 5-10$ being formed together with acetophenone (about 85% of the reaction product)[166]. The lifetime of the ionic substances involved in the reaction in benzene is probably much shorter than in nitroethane.

An analogous linear polymer was also obtained in the polymerisation of PA in the presence of $BF_3.OEt_2$ or CF_3COOH in methylene chloride[39,164]. Here $E_a = 9.7$ kcal mole^{-1} at 0° and 25°C and is independent of the molar ratio of the catalyst and the monomer. In the chain termination reaction, the polymer forms a protonated 1 : 1 complex with an excess of the acid as a result of the interaction of the polymeric cation with the CF_3COO^- counter-ion or another proton transfer reaction. The formation of the complex together with the dependence of the rate constants for the elementary reaction steps (with the exception of initiation) on the length of the polymer chain[39] constitutes the main difference between the polymerisation of PA and that of vinyl monomers.

When PA was polymerised under the influence of BF_3 at room or a reduced temperature in n-hexane, methylene chloride, or 2-bromopropane, a fraction partly soluble in organic solvents was obtained together with a soluble fraction having $\bar{M}_n \simeq 3000$. A linear structure was attributed to both fractions on the basis of infrared spectroscopic data[163]. A linear polymer with $\bar{M}_n = 1000-2000$ was also obtained in the polymerisation of PA in the presence of $AlHal_nR_{3-n}$ in solution or in a suspension in toluene at 30°C [167] or in solution in n-hexane in the presence of $TiCl_4$.[170] The activity of $AlCl_nR_{3-n}$ falls to zero in consequence of the decrease of its electrophilic properties when $n \rightarrow 0$. The yield of the polymer, amounting to 18, 39, and 55% in polymerisation in methylene chloride in the presence of $AlBr_3$, $TiCl_4$, and BF_3 fell when the reaction was carried out under the influence of $BF_3.OEt_2$, $SnCl_4$, and VCl_3 and also in solution in hexane.

In the presence of $BF_3.OEt_2$, *p*-methoxyphenylacetylene forms polymers giving rise to protonated complexes on reaction with an acid. When CF_3COOH was used, only low-molecular-weight products were obtained[38,164]. In the polymerisation of 9-ethynylanthracene, the conversion of the monomer and $\bar{M}_n$ of the products increase with the temperature of the synthesis (the experiments were performed at approximately 20°C and at −70°C).[53] In the course of polymerisation, the active centre isomerises, which leads to the appearance in the polymer chain of allenic 1,6- units and structures (apart from the main 1,2-structures) formed via the Diels–Alder reaction between the growing end of the macromolecule and the initial monomer.

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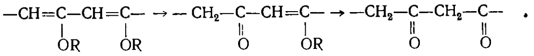
† The catalysts are indicated in square brackets.

In ether, hexane, or methylene chloride at −78°C, alkoxyacetylenes give rise to linear oligomers with $\overline{M}_n$ = 500–600, which are converted into polyketones on subsequent treatment with hydrochloric acid[169]:



$$\underset{\substack{|\\ OR}}{-CH{=}C}-\underset{\substack{|\\ OR}}{CH{=}C}- \rightarrow -CH_2-\underset{\substack{\|\\ O}}{C}-CH{=}\underset{\substack{|\\ OR}}{C}- \rightarrow -CH_2-\underset{\substack{\|\\ O}}{C}-CH_2-\underset{\substack{\|\\ O}}{C}- .$$

Vinylacetylene and its derivatives polymerise[157–161] as a result of the simultaneous dissociation of double and triple bonds with formation of ladder polymers, while only double bonds are involved in the radical process.

The decrease of the reaction rate with time, usually observed in the cationic polymerisation of acetylenes, is not associated with side reactions of the monomer and is due to the deactivation of the catalyst on formation of the catalyst–polymer complex[171]. Because of this, the polymerisation is carried out in the presence of large amounts of catalyst or at elevated temperatures, which promote the dissociation of the complex.

2. Anionic Polymerisation

As noted above, the tendency of alkynes to interact with nucleophilic agents should make them more reactive in anionic polymerisation compared with radical and cationic polymerisation. This is confirmed by the anionic polymerisation of tolane under mild conditions[172], while its thermal polymerisation produces a polymer only at high temperatures[74,75]. Activated electrophilic acetylenes (hexafluorobut-2-yne[173–177], methyl esters of propiolic[178,179], acetylenedicarboxylic, and phenylpropiolic acids, ethyl tetrolate[179], acetylpropiolic anhydride which polymerises also in the presence of alkali[179,180], cyanoacetylenes[181–184], dicyanoacetylene[185], propiolaldehyde[186], propiolamide, tetrolamide, and *N*-methylpropiolamide[187]) polymerise even under the influence of weak nucleophilic agents such as cyanide, thiocyanate, and halide salts.

With increase of the electrophilicity of the substituents at the triple bond (phenylpropiolonitrile[188], cyanoacetylene[181–184,189], and dicyanoacetylene[185,190]), the reactivity of the monomers rises: phenylpropiolonitrile does not change in the presence of tertiary amines, while dicyanoacetylene polymerises readily in their presence even at −73°C.

A method has been proposed for the polymerisation of dialkylamides of acetylene-α-carboxylic acids having the general formula $RC{\equiv}CC(O)NR'_2$ (propiolic or tetrolic acid is best) in aprotic solvents [dimethylformamide (DMF), dimethyl sulphoxide (DMSO), or hexamethylphosphoramide (HMPA)] in the presence of 5–10 mole % of PhSNa, t-BuOK, and tertiary amines with formation of polymers having $\overline{M}_n$ = 2000–3000.[191] The introduction of electron-donating substituents into the propiolamide molecule decreases the reactivity of the monomer; only resinous substances are formed as the products[187].

The reactivity of alkynes has been found to decrease in the following sequences:

$$HC{\equiv}CH > MeC{\equiv}CH > EtC{\equiv}CH\ ^{192} \text{ and}$$
$$MeOOCC{\equiv}CCOOMe > HC{\equiv}CCOOMe > MeC{\equiv}CCOOEt >$$
$$> PhC{\equiv}CCOOMe\ ^{179}.$$

The dimethyl ester of acetylenedicarboxylic acid polymerises even in the presence of a weak nucleophilic agent such as Cl^-, while the methyl ester of phenylpropiolic acid forms a polymer in approximately 1% yield only in the presence of PhSNa.

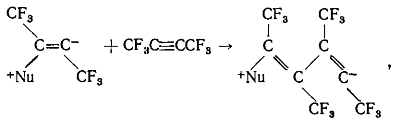
Together with the formation of a linear polyene, the occurrence of cyclotrimerisation processes has been noted[178,188,193–195]. A cyclic trimer is formed on polymerisation of propiolonitrile in the presence of BuLi, but not when sodionaphthalene is used[188]. For the ratio PA : n-BuLi > 20 in HMPA, triphenylbenzene was obtained instead of the linear polyPA.[195]

The polyene structure $-[-CH{=}C(CONH_2)-]_n-$ (polymerisation in bulk in the presence of triethylamine[189]) as well as the heterochain structure $-[-CH{=}CHCONH-]_n-$ (polymerisation in DMF solution in the presence of anhydrous NaCN[187]) has been proposed for polypropiolamide. The structure of polymers corresponding to the dissociation of monomer triple bonds only and analogous to the first of the two described above is produced on polymerisation of the dialkylamides of tetrolic and propiolic acids[196]. In this case the formation of a heterochain polymer is impossible owing to the absence of a mobile hydrogen atom in the amide group. Propiolaldehyde may be converted both into the copolymer $-[-HC{=}C(HCO)-]_x-$ $-[-OCH(C{=}CH)-]_y$ (at −40°C in the presence of NaCN in DMF[186] or at 0°C in the presence of pyridine in THF[114]) and into the homopolymer $-[-OCH(C{=}CH)-]_{x+y}-$ (at −78°C in the presence of pyridine or NaCN in THF[186]).

We shall consider in greater detail certain general features and characteristics of the elementary stages of the anionic polymerisation of acetylenes.

Initiation. Tolane[172], tetrolonitrile[197,198], phenylpropiolonitrile[188], dimethylaminopropynol and 4-dimethylaminobut-3-yn-2-one[168], benzoylpropiolic anhydride[180], acetylpropiolic anhydride[179,180], and dicyanoacetylene[185,190] have been polymerised using for initiation electron transfer from a metalloaromatic complex to the monomer. Such initiation takes place instantaneously and is accompanied by the formation of coloured products.

Polymerisation in the presence of phosphines[185,186,199], amines[184,185,189,199–203], and ammonia[189] presupposes a Zwitter-ionic initiation mechanism, which has been proposed, for example, for the polymerisation of propiolonitrile in the presence of triethylamine[184]. The formation of a dipolar ion is also postulated in the polymerisation of hexafluorobut-2-yne in the presence of Ph_3P, Et_2PH, and Me_3N[199]:



where Nu is a nucleophile.

In the presence of aromatic bases (pyridine, acridine, 3-aminopyridine, etc.), propargyl halides initially form quaternary salts, which then polymerise in the presence of the excess base[204]. Propargyl halides also polymerise in the presence of trialkylarsines, trialkylphosphines, or triarylphosphines[204].

Polar initiators, causing the dissociation of the triple bond of the monomer with formation of carbanions, constitute a large group of substances. The organometallic compounds in this class initiate the polymerisation of disubstituted acetylenes[168] and cyanoacetylenes[185,188,190,197,198]. Weak nucleophilic agents such as alkali metal salts and alkoxides initiate similarly the polymerisation of disubstituted[174–176,179,187,189] and monosubstituted acetylenes[178,180–184,186,187,196]. The polymerisation in the presence of alkali metal salts proceeds simultaneously via radical-anions and carbonium ions[179,205].

An unusual type of initiation reaction is observed in the polymerisation of monosubstituted acetylenes under the influence of strong nucleophilic agents: of 5-ethynyl-2-methylpyridine in the presence of a suspension of sodium[193]; of the mixed anhydrides of acetylene-α-carboxylic and other carboxylic acids[180]; of PA [194,206,207] and cyanoacetylene[183,184,208] in the presence of n-BuLi; of methyl-, ethyl-, and phenyl- acetylenes[192] and p-nitrophenylacetylene[50,209] in the presence of the lithium and sodium salts of DMSO. In this case the acidic acetylenic hydrogen atom is substituted by the metal and chain propagation takes place via the insertion of the monomer in the carbon-metal bond. This mechanism is supported by the polymerisation of acetylenes in the presence of alkali metal acetylides[183,192].

Whereas in non-polar solvents (benzene and toluene) and weakly solvated polar solvents PA does not polymerise in the presence of n-BuLi and gives rise to lithium phenylacetylide in HMP, n-BuLi adds to PA apparently with formation of butylstyryl-lithium, which behaves as the polymerisation initiator[195].

It has been suggested that the polymerisation of ferrocenylacetylene in the presence of a dispersion of sodium, which could not be achieved in the presence of n-BuLi, sodio-dimethyl sulphoxide, and sodionaphthalene, involves the initial dimerisation of the monomer with formation of diferrocenylbutadiyne and subsequent conversion into a ladder polymer[107–110].

Chain propagation. As in the anionic polymerisation of vinyl monomers, for acetylenes there probably exist various types of chain propagation active centres with different reactivities. A study of the polymerisation of acetylenes in DMSO showed[192] that chain propagation takes place at active centres which consist of a solvated complex of the carbanion and the monomer. The addition of a highly dissociated salt ($NaNO_3$, NaI) to the system hindered or stopped the polymerisation. A large excess of the salt suppressed also the initial coordination of the acetylide and the monomer. The results led to the conclusion that chain propagation in a highly solvating medium with a fairly high dielectric constant ($\epsilon \geqslant 23$) takes place preferentially via free anions.

The lack of experimental data on the synthesis of stereoregular polyenes even when the polymerisation is initiated by n-BuLi in a hydrocarbon medium is particularly noteworthy. Individual oligomeric stereoisomers[188] were detected in the polymerisation products of phenylpropiolonitrile in the presence of n-BuLi and sodionaphthalene in THF, which shows that the reaction is not stereospecific.

Chain termination. Chain termination may be due to various causes. A mass-spectrometric study of polyhexafluorobut-2-yne[210], obtained in the presence of CsF, showed that the process is initiated by the F^- ion, while proton transfer from the solvent to the carbanion is responsible for chain termination. Another type of chain termination has been observed in the polymerisation of $DC{\equiv}C{-}CN$.[181,183] According to infrared spectroscopic and NMR data for the low-molecular-weight fraction, the active centre is destroyed as a result of the transfer of deuterium from the monomer to the carbanion.

The absence of factors leading to chain termination presupposes the formation of "live" polymers. Indeed polyacetylene obtained in the presence of the sodium salt of DMSO retains for a long time the ability to form block copolymers with acrylonitrile, ethyl methacrylate, and styrene[192]. The activity series for the vinyl monomers then corresponds to the corresponding series for their anionic homopolymerisation.

Certain experimental facts suggest a decrease of the reactivity of the "live" polymer with increasing length of the polymer chain and an increase of the length of the polyene chain in equilibrium with the monomer when the temperature of the reaction mixture is reduced. Consequently even in "live" polymerisation chain propagation may cease as a result of the attainment of thermodynamic equilibrium in the system[‡]. In this case the change in the rate of polymerisation during the reaction can be explained only by the enhancement of the resonance stabilisation of the anion in the course of the propagation of the conjugated chain[23]. Calculations[202,212–214] confirmed these conclusions.

On the other hand, the observed self-inhibition in the polymerisation of phenylacetylene in the presence of n-BuLi in HMPA has been attributed to the formation of polymer-donor and monomer-acceptor charge-transfer complexes and not to kinetic termination or deactivation of the growing centre[195].

IV. POLYMERISATION OF ACETYLENES UNDER THE INFLUENCE OF TRANSITION METAL COMPOUNDS

Since cyclic and linear oligomerisation and polymerisation of acetylenes frequently accompany one another, the choice of reaction conditions is important for specific synthesis. This section deals mainly with studies whose aim has been to synthesise high-molecular-weight (oligomeric) linear polyene systems.

1. Catalysis by Transition Metal Salts and Their Complexes

Various reactions of acetylenes in the presence of copper(I) salts accompanied by the formation of cuprene analogues insoluble in organic solvents have been studied for a long time[2,6,215]. It has been suggested that polymerisation involving the conversion of PA into a soluble polyene with $M_n = 7000$ in the presence of CuO at 250–350°C proceeds via a stage involving the formation of a linear conjugated polyene which is converted into a three-dimensional product as a result of an intermolecular Diels-Alder reaction[216].

It has recently been established[217] that amine complexes of univalent and bivalent copper salts [CuCl, $Cu(OOCCH_3)_2$] polymerise butyne-2,4-diol and the diacetate derived from it. Linear polymerisation is accompanied by the intermolecular elimination of water or acetic anhydride. The complex spontaneous polymerisation of phenoxyacetylene is apparently accelerated in the presence of CdI_2. [66]

PA has been polymerised in the presence of rhodium salts [$RhCl_2$, [218] $RhCl_3$, [219,220] $RhCl_3.3H_2O$, [221,222] and $Rh(NO_3)_3$ [219]], while in the presence of the complex $RhCl.(PPh_3)_3$ PA, [223,224] hexafluorobut-2-yne[225], and α-ethynylnaphthalene[226] have been polymerised. The reaction is of first order with respect to the monomer and

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[‡] The reversible nature of the polymerisation of acetylene was also observed on carrying out the reaction in the presence of a complex catalyst, where the degree of polymerisation increased with increase of the pressure in the system[211].

the catalyst[219,221], reaching a maximum value in the medium with the dielectric constant $\epsilon = 10$.[219] The activation energy for chain propagation remains constant (approximately 15 kcal mole^{-1}) in media with $\epsilon < 10$, increasing to 20.8 kcal mole^{-1} with increase of ϵ from 10 to 25.1. The dielectric constant was altered by carrying out the polymerisation in different solvents (benzene and its mixtures with ethanol, DMF, and DMSO). Consequently the coordination between the catalyst and solvent molecules determines the polymerisation process. With increase of the concentration of alcohol, there is merely an increase of the number of active centres, which leads to a rise of the rate of reaction without a change in the activation energy. DMF and DMSO, which have been used to obtain media with high dielectric constants, forms stable complexes with the catalysts, which results in an increase of the activation energy and a decrease of the rate of the process.

PA and methylacetylene polymerise over $PdCl_2$ [227] or its complexes with benzonitrile[227,228] and DMSO;[228] poly-(α-ethynylnaphthalene) has been obtained in the presence of the complex $(PdCl_2.PPh_3)_2$.[226] In solutions of rhodium and palladium salts, both catalytic and noncatalytic reactions of acetylenes are possible. The linear oligomerisation of vinyl- and phenyl-acetylenes with formation of σ-organo metallic polyenes has been observed by Temkin and Flid and coworkers[220]. The products are $Cl_mM-[C(R)=CR'-]_{n-1}-CH(R)C(O)R'$ in aqueous solutions and $ClPd-[C(R)=CR'-]_{n-1}-C(R)=C(R')Cl$ with $n = 18-20$ in non-aqueous solutions.

PolyPA with $\overline{M}_n = 3400$ has been synthesised in 67% yield at 20°C in the presence of $[Mo(OCH_3)_2Cl_2]_2$, obtained by dissolving $MoCl_5$ in absolute methanol[229].

The complexes of nickel cyanides with heterocyclic aromatic amines[230] or complexes of the type $NiX_2.(PR_3)_2$, where X = SCN, Cl, Br, or I and R = alkyl, cycloalkyl, aryl, or arylalkyl, have been used to synthesise linear polymers based on various mono- and di-substituted acetylenes[112,226,231-234]. An increase of the catalytic activity of the complexes has been observed in the series $NiCl_2 < NiBr_2 < NiI_2$, PA forming mainly a linear polymer, while propynol gives approximately equal amounts of linear polymers and aromatic trimers[231]. The polymerisation of the dibutyl ester of ethynylboronic acid in the presence of $NiBr_2(PPh_3)_2$ is accompanied by degradative-hydrolytic processes leading to a three-dimensional polymer with the probable structure $[-\overset{|}{C}=\overset{|}{C}-B(OH)OBu]_n$.[235]

In contrast to the complexes $NiX_2.(PPh_3)_2$ discussed above, in the presence of $(PPh_2)_2Ni(C_5H_7O_2)_2$ ethynylferrocene polymerises with difficulty and the structure of the polymer differs from that of the polyethynylferrocenes obtained in the presence of triphenylphosphine complexes or radical initiators[112]. The platinum complexes $(Ph_3P)_2.Pt(R)Cl$ (R = Cl or H), in the presence of which PA,[234,236] 2-methylbut-3-yn-2-ol[237,238], and α-ethynylnaphthalene[226] polymers have been obtained, are less active in the polymerisation of acetylenes.

2. Group VI–VIII Metal Carbonyls

A number of nickel[25,239-243], chromium, molybdenum, and tungsten[242,244] carbonyls or their complexes, for example $Mo(CO)_6$, $Mo(CO)_5.PPh_3$, $Mo(CO)_3.3PyH$, $Ni(CO)_2.(PPh_3)_2$, etc. have been used in the polymerisation of various acetylenic monomers. The polymerisation of 35 different mono- and di-substituted acetylenes in the presence of the complex $Ni(CO)_2.(PPh_3)_2$ has been studied in greatest detail[239,240,245]. The preferential formation of benzene derivatives or linear oligomers of the type $RC{\equiv}C-[-C(R)=CH-]_n-CH=CHR$ and $RC{\equiv}C-[-C(R)=CH-]_n-C(R)=CH_2$, where $n = 0-10$, was determined mainly by the nature of the substituent at the triple bond[239]. Whereas monosubstituted acetylenes with lower alkyl aryl, vinyl, $HOCH_2$, EtOOC, RCO, and RO substituents underwent only cyclotrimerisation, acetylenes with higher alkyl substituents yielded mainly linear oligomers. Only a linear dimer has been obtained from cyclohexylacetylene, while a number of monosubstituted (t-butylacetylene, propargyl chloride, propargyl acetate, cyanoacetylene, 5-chloropent-1-yne, and propiolic acid and its amide) and disubstituted acetylenes (with the exception of but-2-yne-1,4-diol and but-2-yn-1-ol) failed to react. With decrease of the reactivity of the monosubstituted acetylenes (ethers and esters, ketones, vinylacetylene > arylacetylenes > alcohols > higher alkynes > lower alkynes, acetylene ≫ acids), there was an increase of the yield of the linear polymerisation products.

A relation between the rate of reaction and the yield of the polymers on the one hand and the polarity and other properties of the solvents employed in the reaction on the other has not been found in the polymerisation of PA and hept-1-yne[240]. Water, dioxan, THF, acetic acid, and butan-2-one are unsuitable as solvents owing to their ability to form strong coordinate bonds or to decompose the catalyst irreversibly. The reaction is very sensitive to temperature and mixing.

The activity of the catalyst and the direction of the reaction depend also on the nature of the ligands bound to nickel. The replacement of the group R = OPh by R = C_2H_4CN in $Ni(CO)_2.(PR_3)_2$ favours linear polymerisation, while $Ni(CO)_4$ is altogether inactive in the polymerisation of monosubstituted acetylenes[240,246]. However, monomers (propargyl esters of propiolic and undec-10-ynoic acids) are capable of forming activated cyclic intermediates with $Ni(CO)_4$ polymerise in the presence of this complex[246].

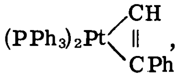
In the polymerisation of PA in the presence of arene-metal tricarbonyls $ArM(CO)_3$, where Ar = toluene or mesitylene and M = Cr, Mo, or W, the reaction is fastest in the presence of molybdenum catalysts in hot aromatic solvents or in bulk at room temperature[242,243], giving a quantitative yield of a linear polyphenylacetylene with a molecular weight of 12 000 (according to gel-chromatographic data).

3. Organic Compounds of Group V-VIII Metals

Under the influence of triphenylchromium, hexafluorobut-2-yne forms only linear polymers[241]. On the other hand, when "dimesitylcobalt"[247] and "diphenylcobalt"[248], which are intermediates in the reaction of cobalt bromide with mesityl- and phenyl-magnesium bromides, are used, but-2-yne and hex-3-yne give rise to a mixture of linear polymers and cyclic trimers. The yield of the polymer and cyclic trimer is directly proportional to the initial concentration of the monomer, but the polymer : cyclic trimer ratio changes at a low temperature from 1 : 17 to 5 : 1 on passing from but-2-yne to hex-3-yne[247]. This is probably associated with the increased steric hindrance in the cyclotrimerisation of hex-3-yne. The yield of poly(hex-3-yne) increases with increase of the concentration of the monomer and falls with increase of temperature, the polymerisation involving a catalytic mechanism under any conditions[248].

Analogous active intermediates are probably formed also when the Iotsich reagents RC≡CMgX are treated with cobalt and nickel chlorides[249].

Acetylenes polymerise in the presence of dicyclopentadienylvanadium[250] and complexes of heterocyclic aromatic amines with dicyclopentadienylnickel[230]. Mainly trialkylbenzenes are formed from propyne, pent-1-yne, and hex-1-yne, PA gives a linear polymer, while disubstituted acetylenes (hept-3-yne, but-2-yne-1,4-diol, and tolane) remain unchanged under these conditions[250]. In the presence of diacrylonitrile- and diacrolein-nickel, phenylacetylene, propargyl alcohol, phenylpropiolaldehyde, and propiolate and acetylenedicarboxylate esters react vigorously to form polymeric products[251].

It has been established[234,236–238] that bistriphenylphosphine complexes of σ-organometallic derivatives of nickel and platinum $(PPh_3)_2Ni(C{\equiv}CPh)_2$,  $(PPh_3)_2Pt\left<\begin{array}{l}CH\\ \| \\ CPh\end{array}\right.$, and *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ catalyse the polymerisation of monosubstituted acetylenes (PA and 2-methylbut-3-yn-2-ol) in bulk and in solution. The less active platinum complexes, in the presence of which the reaction occurs at a fairly high temperature (110–193°C) and is therefore complicated by the thermal polymerisation of the monomer, make it possible to obtain almost exclusively linear polymers. Vinyl-, isopropenyl-, phenyl-, divinyl-, and vinylisopropenyl- acetylenes have been recently polymerised in the presence of the diarene complexes $M(AlCl_4).2C_6H_6$ (M = Co or Ni [252,253])—the so called "alkyl-free organometallic catalysts"[254].

The polymerisation of acetylenes under the influence of catalytic systems based on π-allyl transition metal complexes is of considerable interest. Such complexes were proposed for the first time for the polymerisation of monosubstituted acetylenes by Japanese investigators[255].

In the presence of the π-allylmetal halides $[\pi\text{-(allyl)}.MX]_n$, where allyl = C_3H_5 (allyl), C_4H_7 (but-2-enyl), or C_5H_9 (pentenyl), M = Ni or Pd, X = Cl, Br, or I, and n = 1 or 2, alkylacetylenes (hex-1-yne, hept-2-yne, and oct-4-yne) cyclotrimerise and arylacetylenes (PA) oligomerise[256,257]. The activity in cyclotrimerisation falls in the above series of allyl derivatives.

Polyvinylenes have been obtained from methyl-, phenyl-, vinyl-, and vinylpropenyl-acetylenes under the influence of $(\pi\text{-}C_4H_7NiX)_2$, where X = I or Cl.[258] The reaction takes place quantitatively under mild conditions (25°C, 2 h, molar ratio monomer : catalyst = 30–50) and vinyl- and vinylpropenylacetylenes polymerise exclusively via the triple bond.

PA [259,260] and cyanoacetylene[261] in the presence of di-(π-allyl)nickel and PA in the presence of di-(π-but-2-enyl)nickel[260] form a mixture of cyclic trimers and linear polyenes. The maximum conversion of cyanoacetylene in the temperature range between −30° and 30°C occurs at 30°C. The yield of both the polyene and the cyclic trimer diminishes as the temperature is reduced[261,262].

The polymerisation of vinyl- and isopropenyl-acetylenes in the presence of di-(π-allyl)nickel gives rise to a mixture of soluble and insoluble products[263]. Above 0°C, the main reaction product from isopropenylacetylene is a soluble polymer, while below 0°C an insoluble polymer is formed. The soluble polymer loses its solubility after isolation. The polymerisation involves preferentially the isopropenyl group in the 1,2-position, together with the dissociation of the triple bonds and the formation of small blocks of conjugated double bonds. A polymer consisting mainly allenic units has been obtained from vinylacetylene via the 1,4-addition mechanism. Polymerisation via the triple bond also takes place to a slight extent.

The activity of the π-allyl complexes of nickel decreases in the sequence[257,258] $(\pi\text{-}C_4H_7NiI)_2 > (\pi\text{-}C_4H_7NiCl)_2 > (\pi\text{-}C_4H_7)_2Ni$. The influence of electron-donating (phosphines and amines) and electron-accepting (nickel trichloroacetate, $AlBr_3$, and $TiCl_4$) additives on the polymerisation reaction is extremely varied. In the presence of pyridine and DMF (in the stoichiometric amount or in excess relative to the catalysts), the overall yield of acetylene oligomerisation products in the presence of the $[\pi\text{-(allyl)}MX]_n$ catalysts falls, the cyclotrimerisation processes being retarded in the first place. Triphenylphosphine exhibits a weaker inhibiting activity than amines. Complexes containing more than three PPh_3 molecules per metal atom greatly activate the cyclisation of alkynes[257]. On passing from $(\pi\text{-}C_4H_7NiI)_2$ to its complex with one molecule of $Ni(OCOCCl_3)_2$ (the latter does not catalyse the reactions of acetylenes), triphenylbenzene is formed preferentially from PA instead of the linear polymer. On the other hand, when $(\pi\text{-}C_4H_7NiCl)_2$ is replaced by its complex with 1.5 molecules of $Ni(OCOC.Cl_3)_2$, the rate of cyclotrimerisation of hept-2-yne decreases without a change in the mode of the process[256]. A retardation of the polymerisation of vinylacetylenic hydrocarbons under the influence of Lewis acids has also been noted[258].

When di-(π-allyl)nickel is used, the influence of the additives varies depending on the nature of the monomer. The presence of phosphines does not influence the direction of the reaction of cyanoacetylene and the yield of reaction products[261,262]. On the other hand, the addition of PPh_3 and $TiCl_4$ alters the mode of polymerisation of isopropenylacetylene: the triple bond is dissociated instead of the double bond. The replacement of $(C_3H_5)_2Ni$ by $(C_3H_5NiBr)_2$ has a similar effect[263].

4. Ziegler–Natta Catalysts

The most common organometallic complex catalysts, or Ziegler–Natta catalysts, which are widely used in the polymerisation of olefins, have also found applications in the polymerisation of acetylenes. Depending on the nature of the acetylenic monomer and the reaction conditions, the process can be driven towards the preferential formation of cyclic trimers (benzene derivatives)[7,14,17,18,25] or linear polymers[7,17,18,264–271]. The available data about the influence of reaction conditions on the structural specificity of the polymerisation process are extremely contradictory. When alkynes were polymerised under the influence of catalytic systems based on organoaluminium compounds and titanium derivatives, the maximum yields of cyclic trimers were obtained in the presence of $TiCl_4$.[272–280] It was also noted[281,282] that the reaction in the presence of $TiCl_3$ leads to the formation of linear polymers only, which is inconsistent with other data (see below).

Substituents at the titanium atom have a much stronger influence on the direction of the process than changes in the aluminium component. The $Et_3Al\text{–}(C_5H_5)_2TiX_2$ catalytic systems, where X = Cl or OBu, are relatively ineffective in the linear polymerisation of PA.[283] When $TiCl_4$ in the complex with R_3Al (where R = Et or iso-Bu) is replaced by $Ti(OR')_4$ (where R′ = Et or Bu), the catalytic system becomes inactive in the cyclotrimerisation reaction[282,284–286]. On the other hand, systems of the type $R_2AlCl\text{–}Ti(OR')_4$ are active in cyclotrimerisation and polymerisation[284,286]. These data suggested that, in order to obtain benzene derivatives from acetylenes under the influence of typical Ziegler–Natta catalysts, a halogen atom combined with a transition metal[275] or in one of the catalyst components[284] is necessary. On the other hand, when Et_3Al is replaced by Et_2AlCl in the complex with $Fe(DMG)_2$ (where DMG = dimethylglyoxime), the system becomes almost inactive in the polymerisation of PA.[286] Similarly the effectiveness of the alkylaluminium component in the complex with $Fe(DMG)_2.2X$ (where X = PyH or NH_3) in the linear polymerisation of α-ethynylnaphthalene decreases in the sequence[287] $Et_3Al > (iso\text{-}Bu)_3Al > Et_2AlCl$. A change in the transition metal can affect both the proportions and the structures of the linear and cyclic polymerisation products.

The catalytic activity of the complex catalyst with Et_3Al in the polymerisation of α-ethynylnaphthalene[288] decreases in the following sequence as a function of the transition metal: $Co(Acac)_3 > Fe(Acac)_3 > Cr(Acac)_3 > Ti(OBu)_4 > VO(Acac)_2$, while in the polymerisation of PA [285] the sequence is $Co(Acac)_3 > Cr(Acac)_3 > VO(Acac)_2 > Ti(OBu)_4 > TiCl_2(C_5H_5)_2$.

Whereas the polymerisation of ethynylferrocene in the presence of the $R_3Al–Ti(OBu)_4$ catalytic system leads to the formation of polyenes with $\overline{M}_n = 1000–3500$,[285] there is no polymerisation under the influence of $Et_3Al–TiCl_4$,[289] while in the presence of $(iso\text{-}Bu)_3Al\text{-}VO(Acac)_2$ insoluble and infusible products were obtained; according to infrared spectroscopic data, such products are not formed as a result of the dissociation of the triple bond[290].

The complexes $(iso\text{-}Bu)_3Al–VOCl_3$ and $(iso\text{-}Bu)_2AlCl–VOCl_3$ are less active than $(iso\text{-}Bu)_3Al–TiCl_4$, probably in consequence of the interaction of the oxygen p electrons with the vacant orbitals of vanadium, which lowers its capacity for coordination. The coordination saturation of the vanadium atom on passing from $VOCl_3$ to $V(Acac)_3$ in the above complexes makes them inactive in the formation of linear and cyclic products[291,292]. The reduced activity of the vanadium complexes compared with the titanium complexes is also associated with the greater stability of the former[292]. The stereospecificity of the $(iso\text{-}Bu)_3Al–TiCl_4$ system demonstrated in relation to 1,3,5- and 1,2,4-tri-n-butylbenzenes formed on polymerisation of hex-1-yne, is much higher than that of $(iso\text{-}Bu)_3Al–VOCl_3$,[291] which agrees with the relative stereospecificities of the analogous systems in the polymerisation of propene[293].

Electron-donating additives (PyH, NH_3, THF, etc.) have a marked influence on the properties of catalysts; a limited influence of PyH and Et_3N on the yield and proportions of the final products in the polymerisation of ethynylferrocene has been noted[286]. A decrease of the yields and molecular weights of the PA [283,287,294] and p-iodophenylacetylene[77] polymers have been observed when modified systems comprising Et_3Al with $Fe(DMG)_2.2D$ (where D = PyH or NH_3) and $TiCl_3.D_n$ (where D = PyH and n = 1 or 2) were used. The use of δ-$TiCl_3$ (this modification contains up to 27% $AlCl_3$) instead of α-$TiCl_3$ in the complex with Et_3Al leads to an appreciable increase of the yield of cyclic trimers[294]. The activity of the complex falls with increase of the coordinating capacity of the electron-donating additive[287]. In this connection it is interesting to note that, when the catalytic complex is prepared under appropriate conditions, the acetylenic monomer may form part of the complex as an electron-donating additive[295].

The virtually constant activity of iron, cobalt, and nickel chelate complexes in the polymerisation of acetylenic compounds (regardless of the structure of the ligand) and the influence on the process of the electron-donating additives bound to the catalyst show that the coordination of the monomer or the polymer to the transition metal atom is a significant factor in polymerisation in the presence of Ziegler–Natta catalysts[283,287].

The ratio of the components of the catalytic system is very important for the specific synthesis of linear and cyclic products. This is not surprising, since the formation of the active catalytic complex is associated primarily with alkylation and the change in the valence state of the transition metal[296,297]. Thus, in polymerisation in the presence of the $R_3Al–TiCl_4$ catalytic system, the maximum yield of the cyclotrimerisation products derived from a number of alkynes was noted for the molar ratio Al:Ti = 1–3 (with R = iso-Bu),[276] 3 (with R = Et),[298] 3 (with R = iso-Bu),[282,291,292,299,300] and 2–4 (with R = Et).[274] Whereas in the polymerisation of PA in the presence of $Et_3Al–TiCl_4$ the maximum yield of linear polymers was reached for Al:Ti > 4,[274] in the presence of $(iso\text{-}Bu)_2AlCl–TiCl_4$ linear polymers were not obtained for any Al:Ti ratios in the range from 1/3 to 8;[284] in the presence of $Et_2AlCl–TiCl_4$ with Al:Ti = 3–7 the yield of triphenylbenzenes falls sharply and the main reaction product is a linear polymer[273]. On the other hand, other investigators believe that the optimum ratio for the formation of linear polymers is Al:Ti = 1–3.[269,301–303] In the presence of the $R_3Al–Ti(OBu)_4$ system where R = Et or iso-Bu, no changes were observed in ethynylferrocene for the molar ratio Al:Ti = 1. For higher Al:Ti ratios, up to 20, mainly a linear polymer is formed. On passing from R_3Al to Et_2AlCl and for the molar ratio Al:Ti = 5, only a cyclic trimer is formed[286]. Poly-α-ethynylnaphthalene and polyPA have been obtained in the presence of $Et_3Al–Ti(OBu)_4$ for Al:Ti ratios of 2.86 [288] and 4 [285] respectively. The replacement of $TiCl_4$ by $TiCl_3$ increases the activity of the system in linear polymerisation reactions over a wide range of Al:Ti ratios (from 1 to 10),[75,77,268,272,283,304–309] the use of δ-$TiCl_3$ resulting in an increase of the polymerisation rate constant approximately by a factor of 5 compared with α-$TiCl_3$.[308]

When the nature of the transition metal is altered, the optimum ratio of the catalytic system components for the preferential formation of linear or cyclic products changes. This is mainly because of the ease of reduction of a particular metal. Indeed vanadium halides react with aluminium alkyls much more readily than do titanium halides[296]. In conformity with this finding, the optimum ratios in the polymerisation of hex-1-yne in the presence of $(iso\text{-}Bu)_3Al–TiCl_4$ and $(iso\text{-}Bu)_3Al–VOCl_3$ are respectively Al:Ti = 3 and Al:V = 1.5. With increase of the latter ratio, the yield of the linear polymer rises sharply for an overal conversion of 100%.[291] However, as in the case of olefins[297,298], there are no unambiguous data concerning the valence state of the transition metal in the catalytic complex in the polymerisation of acetylenes. For example, it is believed that the maximum activity of the system with respect to cyclotrimerisation corresponding to Al:Ti = 3 is determined by Ti^{2+} [274] or Ti^{3+}.[292]

The data concerning the influence of solvents on the structure of the reaction products are also contradictory. Donda et al.[274] believe that aromatic solvents promote the cyclisation of PA in the presence of $Et_3Al–TiCl_4$. According to the results of Reikhsfel'd and coworkers[282,310], the nature and amount of the solvent, which is inert with respect to the catalyst (benzene, n-heptane, cyclohexane, n-octane, and isooctane), do not influence the overall yield and the proportions of the 1,2,4- and 1,3,5-trisubstituted benzenes formed in the polymerisation of a number of alkynes in the presence of (iso-Bu)$_3$Al–TiCl$_4$. In the presence of the same catalytic system, no difference was observed between the polymerisations of α-ethynylanthracene in n-heptane and toluene[53]. On the other hand, the yield of cyclic trimers in the polymerisation of PA in the presence of Et$_3$Al–TiCl$_3$ is determined by the type of solvent employed[308]: other conditions being equal, mainly linear polymers (in yields of 84–98%) are formed in aromatic solvents (benzene, toluene, and *o*-dichlorobenzene), while in aliphatic solvents (n-heptane, cyclohexane, and dichloroethane), the products are cyclic trimers (23–90%).

The range of monomers polymerised in the presence of Ziegler–Natta catalysts is fairly extensive: propyne[272,290,295,298], but-1-yne[298 304 311], pent-1-yne[75], hex-1-yne[268,282,284,291,292,304–306,311,312], dodec-1-yne[311], 3,3-dimethylbut-1-yne[299], 3-methylpent-1-yne[313], 4-methylhex-1-yne[306], vinylacetylene[284,300,301], isopropenylacetylene[273], PA,[170,274,283,285,287,295,307,308,314,315], *o*- and *p*-nitro, -chloro-, and -methyl-phenylacetylenes[214], phenyldeuteroacetylene[316], α- [288] and β-ethynylnaphthalenes[303], 9-ethynylanthracene[53], ethynylferrocene[286], cyanoacetylene[317], α-furylacetylene[300], isobutoxyacetylene[318], phenoxyacetylene[302], trimethyl- and triethyl-silylacetylenes[319,320], but-2-yne[298], dec-5-yne[298], methylphenylacetylene[316], and β-iodophenylacetylene[75,77]. Propargyl bromide and 5-ethynyl-2-methylpyridine do not polymerise—the former monomer decomposes the catalyst, while in the presence of the latter the catalyst is not deactivated. According to Makovetskii et al.[300], the pyridine substituent weakens the capacity of the triple bond for coordination. Disubstituted acetylenes show a greater tendency towards the formation of cyclic trimers than monosubstituted derivatives[276,294,316], which can probably be explained by the greater steric hindrance in the formation of the linear polymer chain. When the temperature was reduced, a decrease of the conversion of the monomers[269,283,284,286,291,302,307] and an increase of the relative content of cyclic trimers in the reaction products[294,316] were observed. The yield of cyclic trimers also increases with increase of the degree of conversion of monomers[294,316].

It is known[296,297] that not only the ratio of the components of the catalytic complex but also the state of aggregation of the catalyst and its degree of dispersion in the solvent have a major influence on the structure and properties of the products obtained. In their turn, these parameters depend in many respects on the conditions in the preparation of the catalytic complex (the order in which the components are introduced, the rate of stirring, the temperature and duration of interaction, the absence or presence of a solvent, the absolute amounts of the components, etc.). Thus in the polymerisation of PA in the presence of Et$_3$Al–α-TiCl$_3$ the order in which the components of the catalytic system, the solvent, and the monomer are mixed has hardly any influence on the rate of reaction. However, when δ-TiCl$_3$ is used, a change in the order in which the reactants are introduced (a change from the sequence TiCl$_3$ + Et$_2$Al solution + monomer to the sequence TiCl$_3$ + monomer + Et$_3$Al solution) alters sharply the polymerisation kinetics[316]. In the latter case the monomer is probably actively involved in the formation of other catalytic active centres. This may be promoted by the AlCl$_3$ present in relatively large amounts as an impurity in δ-TiCl$_3$. Similarly the purity of the metal alkyl has a definite influence on the degree of reduction of the transition metal (for example, one must take into account the virtually unavoidable admixture of the highly reducing aluminium hydride in the initial aluminium alkyl component). It is extremely probable that the contradictory nature of many of the data discussed is in fact in many respects determined by the different conditions used in the preparation of the catalyst components and the catalytic complexes based on them as well as different process conditions.

5. Other Catalysts

The linear polymerisation and cyclotrimerisation of acetylenes is catalysed by many systems comprising Group VIII transition metal compounds (with the exception of iron) or their complexes, for example NiCl$_2$, CoBr$_2$, PbCl$_2$, Ru(SCN)$_2$, OsCl$_2$, [Ni(C$_2$H$_4$CN)$_3$.P]$_2$, PdCl$_2$.[P(Bu-n)$_3$]$_2$, and NiCl$_2$.[P(Pr-n)$_3$]$_3$ in combination with hydrides of Group I–IV elements (NaBH$_4$, KBH$_4$, LiH, LiAlH$_4$, B$_2$H$_6$, SiH$_4$, SnH$_4$, etc.)[224,241,321–326].

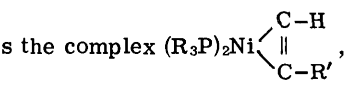
The systems comprising cobalt, platinum, palladium, and osmium proved to be the most active in the polymerisation of hept-1-yne. The valence of the metal is unimportant, but the effectiveness of the organometallic complex is greater than that of an inorganic salt. At high temperatures the process is catalysed even in the absence of a reducing agent[326].

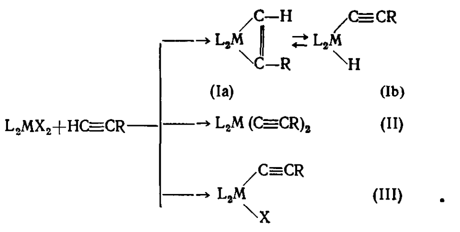
Acetylenes also polymerise under the influence of palladium on charcoal[327] and catalytic systems consisting of an iron halide (FeX$_n$, where X = Cl or Br, and *n* = 2 or 3), and alkali metal acetylide, and a ketone[328,329].

6. The Mechanisms of the Polymerisation Reactions of Acetylenes in the Presence of Transition Metal Compounds

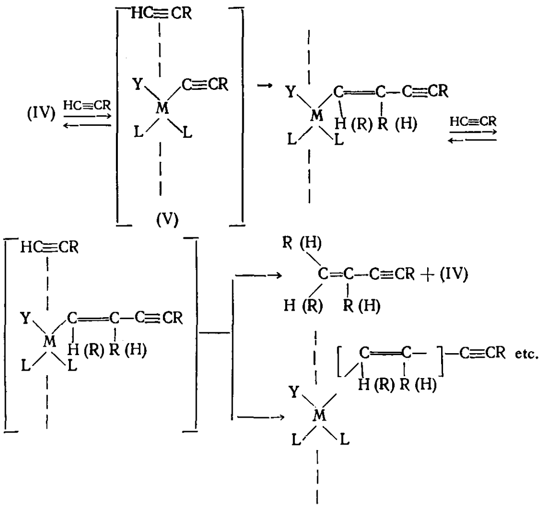
Several mechanisms have been proposed for the cyclic oligomerisation and linear polymerisation of acetylenes, which reflect primarily the wide variety of the catalytic systems employed. However, the contradictory nature or lack of some data on the kinetics and mechanisms of the processes, frequently caused by experimental difficulties (the high rates and heats of reaction[240,330]), make these mechanisms merely hypothetical.

Despite the wide variety of transition metal compounds which catalyse the polymerisation of acetylenes, the first stage in the linear polymerisation and cyclotrimerisation is believed to be coordination of acetylenes to the transition metal of the π-complex type[15,25].

According to Meriweather et al.[240], when Ni(CO)$_2$.(PR$_3$)$_2$ is used, the actual catalyst of the polymerisation of acetylenes is the complex  $(R_3P)_2Ni\left\langle\begin{matrix}C{-}H\\ \Vert\\ C{-}R'\end{matrix}\right.$, in equilibrium with the hydride acetylide (R$_3$P)$_2$Ni(H)C≡CR′. The advantages and disadvantages of this mechanism have been discussed in detail in the literature[14,15,25]. Whereas intermediate acetylides have not been detected in the case of nickel catalysts, a number of acetylides have been isolated in the presence of the less active triphenylphosphine complexes of platinum[236–238]. Possibly the formation of acetylides determines the induction period in polymerisation[234]. The "organometallic" mechanism based on these data can be represented as follows[112,226,236]:

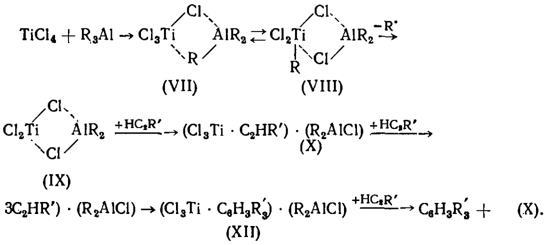


We put (Ib) = (II) = (III) = $L_2M\langle^{C\equiv CR}_{Y}$ = (IV), where M = metal, L = ligand, R = alkyl or aryl, Y = H or C≡CR, and X = Cl, Br, I, or SCN.



The reaction of the phosphine complex of the metal with the alkyne results in the formation of one of the active intermediate products (I)–(III) or their mixture, (IV). Then (IV) reacts rapidly and reversibly with another alkyne molecule to form (V). In the π-complex (V), the triple bond interacts with the p_z orbital of the bivalent metal in such a way that the z axis passes through the centre of the triple bond and the alkyne is disposed parallel to the plane of the complex. The presence in the system of a new π-linked acetylenic unit (V), acting as a kind of Lewis base, compensates the weak shift of the π-electron cloud of the σ-linked acetylenic unit and leads to the formation of (VI). The growth of the polymer chain takes place via the insertion of the coordinated monomer molecule in the ≡C–M bond.

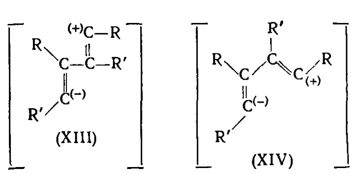
On the basis of the investigations made, Reikhsfel'd and Makovetskii suggested[14,282] that, regardless of the type of catalyst used, the cyclotrimerisation of acetylenes proceeds via a coordination mechanism similar to that proposed earlier for the formation of benzene or cyclooctatetraene derivatives in solutions of nickel complexes[15]. When account is taken of later refinements[292], the proposed mechanism is as follows. When the alkyne RC≡CH molecule interacts with the Ti^{3+} ion, forming part of the two-metal complex with aluminium in proportions of 1 : 1, the complex (VII) is formed with a bridge bond via the R group. The presence of this bond is necessary for the reversible alkylation of titanium to the complex (VIII). The alkylation of titanium is promoted by the fact that the bridge bond via the chlorine atom is energetically more favourable than the bridge bond via the alkyl group. The complex (VIII) contains the extremely unstable Ti–R bond, which dissociates with formation of the complex (IX). The latter reacts with an alkyne molecule to form a new complex (X), which contains, like complex (IX), a coordination-unsaturated titanium atom. In the attack on the complex (X) by two alkyne molecules, an octahedral complex (XI) is produced. According to kinetic data (the second order of the cyclotrimerisation reaction with respect to the monomer[313]), the last stage determines the rate of the entire process. The next stage is the intramolecular exchange of the chlorine atom for the alkyne with a nearly coplanar disposition of all three alkyne molecules and subsequent formation of a benzene ring from them. This liberates two coordination sites in the octahedron, which rearranges back to a square form (XII) with a molecule of the benzene derivative as the ligand. The latter is displaced by a new alkyne molecule with formation of the initial complex (X):



The mechanism discussed above is based primarily on the independence of the cyclotrimerisation reaction (observed by the authors) in different solvents and the identical reactivities in this process of acetylenes with substituents having the opposite effects on the electron density of the triple bond. On the other hand, the mechanism does not explain the simultaneous formation of linear as well as cyclic oligomers and the influence of the nature of the solvent on the ratio of the cyclic and linear products noted in many instances[274,294,308]. The formation of asymmetric 1,2,4-trisubstituted benzenes, the yield of which is sometimes equal to or greater than that of the symmetrical 1,3,5-isomer[277,278,294,308], is also difficult to account for in terms of the "coordination" mechanism. The first order (with respect to the monomer) of the PA cyclotrimerisation reaction[294,308] in the presence of the $Et_3Al-TiCl_3$ system is not consistent with the many-centre character of the "coordination" mechanism.

Many investigators have developed the anionic-coordination mechanism of cyclotrimerisation and linear polymerisation of acetylenes, proposed for the first time by Natta et al.[332]

According to Lutz[14,298], the alkyne is polarised after chemisorption on the catalyst surface. Chain propagation proceeds via the Al–C bond and the direction of the reaction is determined by the configuration of the intermediate complex—(XIII) or (XIV); a linear polymer is formed in the presence of the former and a cyclic trimer in the presence of the latter:

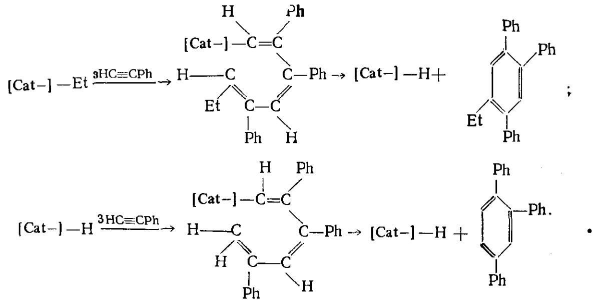


The high selectivity of the cyclisation of disubstituted acetylenes is associated with steric factors. However, this mechanism does not explain the cyclotrimerisation of monosubstituted acetylenes occurring in many instances with high yields.

A study of the reaction of acetylene in the presence of the $Et_3Al-TiCl_4$ system established[333] that ethylbenzene is formed together with benzene. A control experiment showed that the former is not a product of the direct alkylation of benzene under the influence of Et_3Al. This suggested that the cyclotrimerisation proceeds with participation of the M–C bond and the intermediate formation of linear products.

There is no doubt that, as in the polymerisation of olefins in the presence of Ziegler–Natta catalysts, the reactions of acetylenes are initiated by the insertion of the monomer molecule in the M–C bond of the complex catalyst. It has been established by NMR for the $Me_2AlCl-(C_5H_5)_2TiCl_2$ catalytic system[334] that PA is inserted in the Ti–Me bond. The monomer, activated on formation of the π-complex[15], undergoes the *cis*-dissociation of the triple bond during the addition to the M–C bond, as shown by the chain structures of the polyenes synthesised[335–337]. Measurements of the electrical conductivities of reaction mixtures with different compositions have shown that the PA polymerisation reactions in the presence of many Ziegler catalysts are ionic[285].

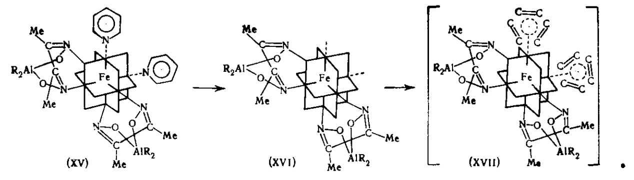
Data obtained in two investigations[294, 308] on the polymerisation of PA in the presence of $Et_3Al-TiCl_3$ are consistent with the anionic-coordination mechanism. The independence of the rate constant for the polymerisation of PA in n-heptane of the yield of cyclic trimers and the first order of the reaction with respect to the monomer show that the mechanism of the formation of cyclic products in the polymerisation of PA in the presence of Ziegler systems is determined by the abstraction of the linear trimer from the catalystic centre with ring closure and not by the simultaneous step involving the interaction of three monomeric units:



The presence of the ethyl group in triphenylbenzenes confirms this mechanism. The preferential formation of cyclic products when the polymerisation is carried out in aliphatic hydrocarbons and of linear polymers in aromatic solvents is associated with the donor–acceptor interaction of the aromatic solvents with the growing chain, which hinders the formation of a conformation suitable for cyclisation. Furthermore, one cannot rule out the possibility of the formation of complexes by aromatic solvents with the titanium component of the catalyst[49, 338–341], which would also hinder cyclisation. The strong inhibiting effect of Et_3Al on the cyclisation process may be explained as follows: by the capture of the end of the polyene chain due to the counteraction by the free Et_3Al on the $TiCl_3$ surface; by the donor–acceptor interaction of Et_3Al with the polyene chain; by the possibility of the formation of Et_3Al as an agent transferring to the chain the secondary active centres [Cat–]–Et, on which the growing chains have an "alkyl" tail which sterically hinders cyclisation.

However, one should note that the homogeneous catalytic system $R_3Al-NiCl_2$ is formed in both aliphatic and aromatic solvents, while polarisation takes place only in the latter[288]. The aromatic solvent probably plays in this case the role of a ligand with π-donor properties, increasing the possibility of dative interaction between the transition metal and acetylene.

Simionescu et al.[226] consider the complex $Fe(DMG)_2.2PyH$ as an octahedral chelate system, which gives rise to a new complex (XV) by reaction with R_3Al. The formation of (XV) was confirmed experimentally by the detection of the RH produced. The aluminium in (XV) decreases the electron density of the Fe–N chelate linkage, which is enhanced by the π-electron system of PyH. In this connection, one should consider the above activity series of aluminium alkyl components[226, 287, 288]. On heating (90°C, 15 min), the complex (XV) is converted into the polymerisation catalyst (XVI) proper. The electron deficiency of the Fe–N linkage is compensated in (XV) by the six alkyne molecules forming two three-unit aromatic systems of type (XVII). The subsequent dissociation of the triple bond leads to the formation of the polyene:



In contrast to the polymerisation mechanisms already examined, where chain propagation takes place (by analogy with vinyl polymerisation) as a result of the addition of the triple bond to the active terminal bond, in the presence of $RhCl.(PPh_3)_3$ PA behaves as a bifunctional monomer. C≡C and ≡C–H behaves as functional groups. Chain propagation is the result of the successive addition of the ≡C–H bond in one monomer molecule to the C≡C bond in another under the coordinating influence of rhodium, as shown by the formation of *trans*-1,4-diphenylbutenyne[223].

The catalytic activity of π-allyl compounds is apparently in many respects determined by their stability, which depends on the nature of the metal and the ligands linked to it[254]. The presence of π-allyl groups is not an obligatory condition for the activity of the complex; the creation of a specific state of the transition metal and a definite degree of its stabilisation are important[257]. The oligomerisation of acetylenes on π-allyl halides is described by first-order kinetic equations with respect to the monomer. The reaction order with respect to the catalyst varies as a function of its nature: it is 0.5 in cyclotrimerisation on π-crotylnickel chloride and unity on the monomeric π-pentenylnickel iodide[257]. The acetylenic monomer initially displaces the allyl ligand from the catalyst (identification of diallyl) with formation of formally univalent (from π-allylmetal halides)[260, 261] or zerovalent nickel[256, 257]. Linear polymerisation takes place via the insertion of the monomer in the M–C σ bond and subsequent chain transfer to the monomer[257, 260] or via insertion in the metal hydride linkage[261].

The hypothetical mechanism of catalysis by a Group VIII transition metal salt and a hydride reducing agent presupposes the reduction of the ion to the lowest valence state with formation of the metal hydride, which in its turn gives a complex with two and more monomer molecules[325]. In this complex the metal atom behaves as an agent transferring hydrogen from one monomer molecule to another.

In the light of recently published interesting data on the polymerisation of a number of acetylenes in the presence of Group VIB arenemetal tricarbonyls[242,243], the "cyclobutadiene" mechanism[15], which has not apparently been considered for the explanation of the linear polymerisation of acetylenes, has attracted attention. An intermediate ladder compound having the cyclobutane structure, which is rapidly and quantitatively converted into linear polyPA following the addition of the catalyst, has been isolated from the products of the initial stage of the polymerisation of PA. Dewar hexamethylbenzene has been detected in the reaction medium in the polymerisation of but-2-yne[242,243]. These findings suggested that a series of consecutive [2 + 2] cycloadditions initially result in the formation of ladder polymers, which are then converted into higher-molecular-weight linear products, probably via a series of metathetical reactions of the olefins with subsequent isomerisation of the electronic structures of the final compounds.

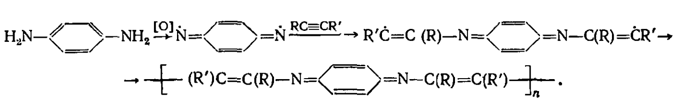
V. COPOLYMERISATION OF ACETYLENES

The copolymerisation of various acetylenic monomers with one another is closest to the homopolymerisation of acetylenes as regards the process mechanism and the properties of the products. As in homopolymerisation, in the copolymerisation of alkynes in the presence of radical initiators[38], cationic catalysts[342], homogeneous and heterogeneous Ziegler–Natta catalysts[343], and catalytic systems comprising Group VIII transition metal compounds and the hydrides of Group I–IV elements[323,324], only copolymers with a low molecular weight have been obtained regardless of reaction conditions. Possibly alternating copolymers are formed in the copolymerisation of *p*-chlorophenylacetylene with *p*-methoxyphenylacetylene and of cyanoacetylene with phenoxyacetylene[38].

The thermal copolymerisation of mono-,and di-acetylenes (PA and *p*-diethynylbenzene) in the range 150–300°C leads to infusible insoluble, and thermally stable copolymers with low electrical resistivities[32–34]. In the catalytic copolymerisation of mono- and di-ethynyl derivatives, the structure of the product is determined by the nature of the diacetylene monomer and the reaction conditions. Whereas the copolymers of PA with *p*-diethynylbenzene contain polyene sections (polyenisation process) together with polyphenylene sections (polycyclotrimerisation process)[26,330,344–348], hepta-1,6-diyne copolymerises with PA under the same conditions via the C≡C bond of the intermediate hept-1,6-diyne dimer, namely 5-(pent-1-ynyl)indane[330,346–349]. Unusual copolymers consisting of polyene or polyene and acene fragments are formed in the homopolymerisation of propargyl propiolate in the presence of $Ni(CO)_4$ [246] or on thermal homopolymerisation of conjugated diynes[26].

The product of the radiation-chemical reaction obtained on irradiation of an acetylene–carbon tetrafluoride mixture by fast electrons at room temperature is apparently a polyvinylene in which some of the hydrogen atoms in the chain have been substituted by fluorine atoms[350]. The fluorine content in the polymer increases with increase of the CF_4 concentration in the initial mixture and varies from 14 to 40 wt.% when the $CF_4 : C_2H_2$ ratio changes from 1 : 1 to 50 : 1 respectively.

The introduction of acetylenic monomers into the reaction system where aromatic compounds undergo polycondensation via a radical mechanism leads to the formation of soluble coloured paramagnetic copolymers. Thus macromolecules containing aromatic and acetylenic units have been obtained by the reduction of aromatic bisdiazonium salts with titanium trichloride in the presence of phenylacetylene, propargyl alcohol, and acetylenedicarboxylic acid[351–353]. The oxidation of aniline and *p*-phenylenediamine by cerium(IV), iron(III), and vanadium(V) salts in the presence of propargyl alcohol, acetylenedicarboxylic acid and its dimethyl ester gives rise to a copolymer via the mechanism[354]

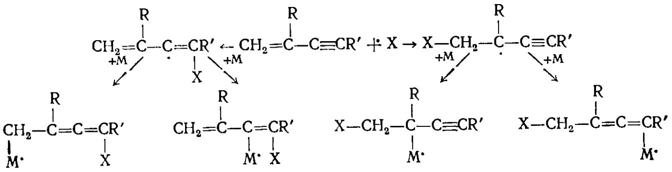


Copolymers containing polyphenylene and polyvinylene fragments are formed when the acetylenic monomer is introduced into the lithium–*p*-dichlorobenzene system in THF solution[355].

The block copolymerisation of polyvinylenes (polyacetylene, polyPA, and polytolane) with electron-accepting vinyl monomers (maleic anhydride, fumaronitrile, and acrylonitrile), occurring in solution and in the melt at 180–200°C, has been investigated[356–360]. A reaction mechanism has been proposed, consisting in the thermal excitation of the charge-transfer complex of the polymer and the monomer to a triplet state at the initiation stage followed by the decomposition of the complex with hydrogen transfer and the formation of polymeric radicals activated by paramagnetic centres and behaving as centres for the growth of macrochains. When polyarylvinylenes are added to vinyl monomers in catalytic amounts, the homopolymerisation of the latter is initiated[361–363].

However, the copolymerisation of acetylenes with olefinic monomers is of greatest theoretical and practical interest. The theoretical interest arises primarily from the determination of the causes of the deactivation of the growing centre on polymerisation of acetylenes and the practical interest is due to the creation of new types of polymeric materials combining the properties of conjugated (high thermal stability and resistance to thermal oxidation, semiconducting properties) and saturated polymers (solubility, fusibility, etc.). It has been noted[364–366] that the set of properties characteristic of polyconjugated systems is manifested to a much greater extent when the conjugated blocks in the macromolecule are separated by fairly long non-conjugated sections. It has been suggested that the copolymers of dicyanoacetylene with vinyl monomers be used in articles where both semiconducting properties and thermal stability are needed (thermoelectric devices, transistors, solar batteries, the casings of rockets, etc.)[367] and that the copolymers of polyvinylenes with ethylene and propene be used for the manufacture of synthetic paper[368].

Studies on the synthesis of rubbers with unsaturated units to facilitate their vulcanisation have been made for a long time[369–371]. The aim of many, particularly the early investigations of the copolymerisation of ethynyldimethylvinylmethanol with dienes[372–377], vinylpyrrolidinone, vinylcaprolactams[378], and 2-methyl-5-vinylpyridine[379] has been to obtain the final products. Price and McKeon[156] proposed the following mechanism for the copolymerisation of vinylacetylenes with acrylonitrile, styrene, isobutene and 2-vinylpyridine (M):



(XVIII) (XIX) (XX) (XXI)

R=R′=H; R=H, R′=Et; R=Me, R′=H; R=Me, R′=Et.

The polymerisation takes place mainly with formation of structures of type (XX), but the monomers with R = Me and R′ = H are partly converted also into structures of type (XIX) or (XXI) [(XVIII)] respectively.

The radical copolymerisation of isoprene with vinylacetylene takes place preferentially and with trimethylvinylethynylsilane exclusively via the double bond of the acetylenic monomer[380]. According to infrared spectroscopic data, isopropenyl- and vinyl-acetylenes are combined into ternary copolymers with ethylene and propene as a result of the dissociation of the triple bond when the reaction is carried out in the presence of $EtAlCl_2$–$VOCl_3$ (or VCl_4). [381, 382] According to the available data on the cationic polymerisation of vinylacetylene[158–161], the copolymerisation of vinylacetylene with isobutene in the presence of BF_3 [369] also probably proceeds via the triple bonds of the acetylenic monomer.

Thus the problem of the structures of the copolymers of the vinyl- and isopropenyl-acetylene series is controversial. As for the data on the homopolymerisation of monomers of this type discussed above, the formation of soluble products is attributed both the the involvement in the reaction of only double or triple bonds of one molecule of the acetylenic monomer[130, 126] and of the triple bond of one molecule and the double bond of another[130, 378]. In the former case linear and in the latter cyclolinear copolymers should be formed.

The copolymerisation of *p*-ethynylstyrene with styrene[113, 383] or of propargyl esters of acrylic, methacrylic, and itaconic acids with *N*-vinylpyrrolidinone and *N*-vinylcaprolactam[89, 384, 385] in the presence of radical initiators probably proceeds preferentially via the double bonds. The number of triple bonds involved in the reaction increases with increasing temperature of the synthesis and at advanced stages of the reaction, which results in the formation of cross-linked products. Under the same conditions, 1,4-di-*p*-chlorophenoxybut-2-yne does not copolymerise with styrene[82].

The explosive copolymerisation of ferrocenylacetylene with chloroprene which could not be prevented by the addition of hydroquinone and which was accompanied by the liberation of iron and HCl, has been observed at 85–90°C. Under the same conditions, ferrocenylacetylene and isoprene failed to react. It is suggested[386] that the degradative processes are associated with the intermediate formation of an unstable α-chlorovinylferrocene.

Dehalogenation of dihalogenomaleic anhydride in the presence of vinyl monomers can serve as a method for the preparation of copolymers with the acetylenedicarboxylic anhydride units[79]. The synthesis of ternary copolymers has been described: acetylene–ethylene–propene[387, 388], acetylene–methylacetylene–propene[389], ethynyldimethylvinylmethanol–butadiene–styrene (or acrylonitrile)[370, 390], $CH_2{=}C(R)C{\equiv}CH$ (where R = H, alkyl, cycloalkyl, or aryl) with 1-mono-olefins[381, 382] and other similar systems[391], hex-1-yne–cyclohexane–sulphur dioxide[392], and PA–cycloheptene–sulphur dioxide[392].

In the statistical copolymerisation of acetylenes, the preferential interaction of the vinyl monomer is usually noted[388, 393–396], which is due to the different reactivities and coordination capacities of the comonomers. Possibly the formation of the copolymer only at a high concentration of the Ziegler catalytic system is associated with the latter factor[397]. However, PA is more active in radical copolymerisation with vinyl chloride[398], vinylidene chloride[399, 400], acrylonitrile[401], and maleic anhydride[402].

The alternating copolymerisation of PA [403] and its *p*-dimethylamino-derivative[50, 404] with maleic anhydride presupposes, like the alternating copolymerisation of vinyl monomers, the preliminary formation of donor–acceptor complexes of the comonomers. The change in the composition of the copolymer as a function of the proportion of the monomers in the initial mixture shows, according to the author[402], that maleic anhydride does not form a stable complex with PA. On the other hand, thermochemical studies and ESR, NMR, and infrared spectroscopic data have shown[360, 405, 406] that the copolymerisation of PA with maleic anhydride proceeds with formation of polyphenylene blocks. One cannot rule out the possibility that the first reaction stage consists mainly in the formation of poly-PA with subsequent addition of maleic anhydride units.

The block copolymers of acetylenic monomers can be obtained in different ways. When PA was added to live polyisoprene with a molecular weight up to 500 000, a block copolymer with the molecular weight of the polyene block up to 10 000 was obtained[407]. The opposite sequence is also possible: the addition of monomers to live polyacetylene chains[192]. When ethylenic and acetylenic monomers were introduced alternately into the reactor containing complex initiators, it was possible to obtain copolymers containing up to 10% of acetylenic hydrocarbons[388, 389]. Block copolymerisation can occur also with simultaneous supply of the comonomers to the catalyst, as happens in the interaction between acetylenes and olefins in the presence of Et_3Al–$TiCl_3$ [408] or (iso-Bu)$_3$Al–$VOCl_3$.[409–411] The intense colour of the copolymer after the complete separation of the ferrocenylacetylene homopolymer suggests the possible block copolymerisation also of the ferrocenylacetylene–isoprene pair in the presence of radical initiators and (iso-Bu)$_3$Al–$TiCl_4$. [397, 412] The possibility of the formation of block copolymers of olefins with acetylenes even at a low concentration of the latter is due, according to Matkovskii[413] primarily to the preferential adsorption of acetylenes by the active centres and the difference between the rate constants for the homopolymerisation of the comonomers. Dimethyl- and ethylmethyl-ethynylmethylamines deactivate the active centres much more markedly than PA, probably owing to the additional involvement of the amino-group in the reaction[411]. An increase in the content of the acetylenic comonomer in the initial mixture reduces the rate of copolymerisation, the yield of the copolymer, and its molecular weight[409–411].

The ability of cyanoacetylene to polymerise under the influence of amines[189] has been used to synthesise graft copolymers. The reaction was carried out by adding cyanoacetylene to a solution of the polymeric initiator, which consisted of a homopolymer of 2-vinylpyridine or the copolymers of 4-vinylpyridine and 2-dimethylaminoethyl methacrylate with vinyl monomers[184].

Thus, despite the inhibiting properties of acetylenic monomers in radical[401, 414, 415] and ionic[409–411, 413] polymer-

Table 1. Conditions governing the preparation of binary acetylenic copolymers.

Acetylenic comonomer	Second comonomer	Initiator	Solvent	Temperature, °C	References
1	2	3	4	5	6
Acetylene[a]	Propyne	$NiCl_2$—$NaBH_4$, $PtCl_4$—B_2H_6, $OsCl_3$—$LiAlH_4$	THF, acetonitrile	26—35	323
	But-1-yne	$NiBr_2$—$NaBH_4$	THF	26	323
	Hept-1-yne	$CoCl_2$—$NaBH_4$, $PhCl_3$—LiH	THF	26—35	323
	Phenylacetylene	$Pd(NO_3)_2$—SiH_4	Ethanol	40	323
	Propargyl alcohol	$RuCl_3$—KBH_4	Dioxan, ethanol	~35	323
	Ethylene	$(iso\text{-}Bu)_3Al$ - $VOCl_3$	n-Heptane	20	410
	Propene	Et_3Al—$TiCl_3$	n-Heptane	50	409
		Et_3Al—$3TiCl_3 \cdot AlCl_3$	n-Heptane	70	388
		Et_3Al—$3TiCl_3 \cdot AlCl_3$	Petrol	50	388
		$TiCl_3$—$LiAlH_4$	Petrol	150—160	389
	Buta-1,3-diene	Et_2AlCl - Ni naphthenate	Toluene	20—30	395
		Et_3Al—$TiCl_4$	n-Heptane	~50	417
	Styrene	Et_3Al—$TiCl_4$	Chlorobenzene	70—75	418
Propyne	But-1-yne	$(iso\text{-}Bu)_3Al$ - VCl_3	Benzene	12.8	343
	Pent-1-yne	$(iso\text{-}Bu)_3Al$ - VCl_3	Benzene	12.8	343
	Propene	Et_2AlCl—$CrCl_3$[b]	—	77	389
	Isobutene	BF_3	Petroleum ether	—60	394
	Buta-1,3-diene	Et_3Al—$TiCl_3$	n-Heptane	50	408
	SO_2	H_2O_2	Paraldehyde	~20	419
But-1-yne	Phenylacetylene	Et_3Al—$TiCl_3$	Benzene	30	343
	Isobutene	BF_3	Petroleum ether	—10	394
	SO_2	H_2O_2	Paraldehyde	~20	419
Pent-1-yne	Isobutene	BF_3	Petroleum ether	—10	394
	SO_2[c]	H_2O_2	Paraldehyde	~20	419
	SO_2[d]	Ascaridol	Ethanol	~20	421
3-Methylbut-1-yne	Isobutene	BF_3	Petroleum ether	—10	394
Hex-1-yne	Methyl acrylate	BP	—	60	401
	Acrylonitrile	BP	—	60	401
	SO_2	H_2O_2	Paraldehyde	~20	419
Vinylacetylene	Isobutene	BF_3	—	—100	369
	Acrylonitrile	AIBN	—	60	156
Isopropenylacetylene	Acrylonitrile	AIBN	—	60	156
	2-Vinylpyridine	AIBN	—	60	156
Propargyl alcohol	Vinyl chloride	AIBN	THF	70	398
Propiolaldehyde	Styrene	AIBN	—	60	422
	Methyl methacrylate	AIBN	Benzene	60	423
Cyanoacetylene	Phenoxyacetylene	—	—	43	38
	Acrylonitrile	NaCN	DMF	—40 — ~20	183
Phenylacetylene	Ferrocenylacetylene	$AlCl_3$	n-Heptane	—70	342
	Ethylene	Et_3Al—$TiCl_3$	n-Heptane	50	408
		$(iso\text{-}Bu)_3Al$ - $VOCl_3$	n-Heptane	20	411
	Propene	Et_3Al—$3TiCl_3\ AlCl_3$	n-Heptane	70	388
		Et_3Al—$MoCl_3(MoCl_5)$	n-Heptane	100	418
	Isobutene	$AlCl_3$	EtCl	—78	393
	But-1-ene	Et_3Al—$TiCl_3$	n-Heptane	60—65	418
	Pent-1-ene	Et_3Al—$TiCl_3$	Benzene	50—70	418
	Styrene	AIBN	—	60	424, 425
		BP	—	60	414
		1-Azobiscyclo-hexane-1-carbonitrile	—	60	401
	Vinyl chloride	AIBN	THF	70	398
	Vinylidene chloride	Radical	—		399, 400
	Methyl acrylate	BP	—	60	401, 414
	Methyl methacrylate	AIBN	—	60	424—426
		AIBN, photochemically	—		427
		—	—	150	428
	Ethyl methacrylate	AIBN	—	60	429
	n-Propyl methacrylate	AIBN	—	60	429
	n-Butyl methacrylate	AIBN	—	60	429
	Isobutyl methacrylate	AIBN	—	60	429
	Vinyl acetate	BP	—	60	414
	Maleic anhydride	—	—	150	360, 405, 406
		^{60}Co γ-radiation	Acetone	30	402
		AIBN	Acetophenone	98	403
		AIBN, photochemically	Ethyl methul ketone	4—6	403
		—	—	98	403
	Acrylonitrile	BP	—	60	401, 414
	2-Vinylpyridine	BP	—	60	414
	Fumaronitrile	—	—	170	405, 406
	SO_2	H_2O_2	Paraldehyde	~20	419
		Ascaridol	Ethanol	~20	421
n-$RC_6H_4 \equiv CH$	*p*-Methoxyphenylacetylene (R = Cl)	t-Butyl peroxide	—	120	38
	Styrene (R = Me, MeO, Cl, Br, or NO_2)	AIBN	—	60	424
	Methyl methacrylate (R = Me, MeO, Cl, Br, or NO_2)	AIBN	—	60	424
	Maleic anhydride (R = Me_2N)	AIBN	Benzene	60	50, 404

Table 1 (continued).

Acetylenic comonomer	Second comonomer	Initiator	Solvent	Temperature, °C	References
1	2	3	4	5	6
Ferrocenylacetylene	Isobutene	BF_3	CH_2Cl_2	—40	430
	Isoprene	(iso-Bu)$_3$Al - $TiCl_4$, t-butyl peroxide or Co(Acac)$_2$	Toluene	20	397
			o-Xylene	150	412
2-Ethyl-1-vinylacetylene	Acrylonitrile	AIBN	—	60	156
	2-Vinyl pyridine	AIBN	—	60	156
diphenylacetylene	Styrene	BP	—	60	401
	Methyl acrylate	BP	—	60	401
	Acrylonitrile	BP	—	60	401
Hexafluorobut-2-yne	1-Chloro-1-fluoro-ethylene	$(NH_4)_2S_2O_8$—$Na_2S_2O_5$	Emulsifier	20	431
	1,1-Difluoro-3-methylbutadiene	$K_2S_2O_8$; pH = 10.2	»	50	431
Dicyanoacetylene[b]	Styrene	AIBN	THF	55	99, 367
Butyne-1,4-diol	Acrolein	*p*-$MeC_6H_4SO_3H$	—	~20	432
		$BF_3\cdot OEt_2$, $SnCl_4$, $FeCl_3$	—	20	433
ROOC — C≡C — COOR′	Vinyl chloride (R = Me, R′ = H)	BP	Methanol	60	434
	Methyl acrylate (R = Me, R′ = H)	BP	Benzene	60	434
	Vinyl acetate (R = R′ = Me)	BP	—	60	434
	Isobutene (R = R′ = Et)	H_2O_2	—	60	434
	Vinyl chloride (R = R′ = Et)	H_2O_2	—	60	434
	Ethyl vinyl ether (R = R′ = Et)	BP	—	60	434
	Methyl methacrylate (R = R′ = Et)	BP	—	60	434
	Vinyl acetate (R = R′ = Et)	BP	—	60	434
p-Diethenylbenzene	Styrene	AIBN	—	60	435
	Methyl methacrylate	AIBN	—	60	435

[a] There is a possibility of the copolymerisation of acetylene with mono-olefins at 40–150°C in DMF under the influence of catalytic systems, consisting of inorganic and organic cobalt or nickel salts and alkali metals or their acetylides[416], and also of the copolymerisation of acetylene or other alkynes with dienes in hydrocarbon solvents at 50°C under pressure in the presence of catalysts of the Ziegler–Natta type[417].

[b] Transition metal halides mixed with lithium and aluminium alkyls, aluminium halide alkyls, or aluminium hydrides can serve as catalysts[389].

[c] Copolymers of hept-1-yne have also been obtained under these conditions[419,420].

[d] Copolymers of non-1-yne, cyclohexylpropyne, and pentadec-1-yne have also been obtained under these conditions[421].

[e] The copolymerisation with other monomers under the influence of radical or ionic initiators is also possible[367].

isation of vinyl monomers, it has been possible to obtain different types of copolymers of acetylenes with olefins (Table 1).

From kinetic studies of the radical polymerisation of styrene and methyl methacrylate in the presence of PA and its derivatives, Higashiura and Oiwa[424,426] regard acetylenes as highly effective inhibitors and not as comonomers. The inhibiting activity of acetylenes is associated primarily with the resonance stabilisation of the terminal growing chain radical and the activity of the acetylenic radicals should decrease sharply with increase in the size of the conjugated block to which the active centre is linked. Bearing in mind that the probability of the formation of radicals of this type should depend on the concentration of the acetylenic monomer in the reaction mixture and on the corresponding reaction rate constants, Uzbekova and Razumovskii investigated the radical copolymerisation of *p*-diethynylbenzene[435] and PA [425] with styrene and methyl methacrylate using reaction mixtures with a low content of the acetylenic monomer. Their data show that the acetylenes investigated can be regarded as comonomers with a weak inhibiting activity.

Zaitsev et al. proposed an equation for the determination of the composition of the copolymer[436], taking into account the characteristics of the radical copolymerisation of acetylenes noted above, i.e. the difference between the reactivities of the radicals $-CH{=}\dot{C}R$ and $-CH{=}C(R)-\dot{C}H{=}CR$:

$$\frac{d[M]}{d[X]}=\frac{r_X[X]/[M]+r_Xr_M+r_M[M]/[X]+1}{2r_X[X]/[M]+1}, \tag{1}$$

where $r_M = k_{MM}/k_{MX}$, $r_X = k_{XX}/k_{XM}$, and M and X are respectively the vinyl and acetylenic monomer. Table 2 shows (the copolymerisation conditions are indicated in Table 1) that the copolymerisation constants r_M calculated from the classical equation and from Eqn. (1) on the basis of the same experimental data hardly differ, while the values of r_X differ appreciably, as was to be expected.

Table 2. The copolymerisation constants for acetylenic and vinyl monomers.

Acetylenic comonomer (X)	r_X	Vinyl comonomer (M)	r_M	References
n-Butylacetylene	0	Methyl acrylate	11.2±2	401
	0	Acrylonitrile	5.4±0.3	401
Vinylacetylene	0.60±0.02	Acrylonitrile	0.13±0.01	156
	0.13	Isobutene	8.0	369, 400
Isopropenylacetylene	0.47±0.01	Acrylonitrile	0.33±0.01	156
	0.55±0.01	2-Vinylpyridine	1.65±0.05	156
Propargyl alcohol	1.0	Vinyl chloride	2.3	398
Propiolaldehyde	0.21	Styrene	0.32	422
	0.27±0.04	Ditto	0.62±0.02	401
	0.47±0.1	Methyl methacrylate	0.65±0.02	436
	0.20±0.02		1.5±0.03	427
Phenylacetylene	—	Ditto	0.81±0.1	425
	0.05	”	0.85±0.1	436
	0.23±0.03	Ethyl methacrylate	2.1±0.1	429
	0.22±0.02	n-Propyl methacrylate	1.4±0.1	429
	0.21±0.02	n-Butyl methacrylate	1.7±0.2	429
	0.27±0.02	Isobutyl methacrylate	1.9±0.1	429
	0.36±0.02[a]	Styrene	0.34±0.1	425
	0.84±0.1	”	0.36±0.04	436
	0.33±0.05	Acrylonitrile	0.26±0.03	401
	0.69±0.04	”	0.30±0.02	436
	0.2±0.05	2-Vinylpyridine	4.0±0.7	414
	0.32±0.15	”	4.0±0.2	436
	3.0	Vinyl chloride	0.2	398
	1.4	Vinylidene chloride	0.1	399, 400
	0.50±0.05	Maleic anhydride	0.05±0.05	402
2-Ethyl-1-vinyl-acetylene	0.63±0.4	Acrylonitrile	0.17±0.01	156
	0.6±1	2-Vinylpyridine	1.5±0.5	156
Diphenylacetylene	0	Methyl acrylate	55±5	401
	0	Acrylonitrile	13.6±1.0	401
Dicyanoacetylene	0	Styrene	1.4	99
p-Diethyny benzene	—	Methyl methacrylate	0.606±0.15[b]	435
	—	Ditto	0.60±0.1	436
	0.74±0.02[a]	Styrene	1.18±0.1[b]	435
	0.87±0.1	”	1.15±0.1	436

[a] Calculated by Zaitsev et al.[436] from the data of Uzbekova and coworkers[425,435].

[b] r_M was calculated from the differential equation for the composition of a copolymer of bifunctional monomers[437].

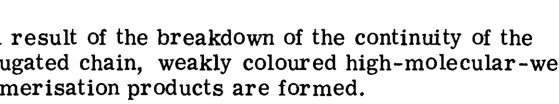
VI. THE STRUCTURES AND ELECTROPHYSICAL PROPERTIES OF ACETYLENIC POLYMERS

The data on the kinetics of the polymerisation of a number of acetylenes discussed above indicate a monomolecular mechanism of chain termination and the independence of the molecular weight of the conditions of the synthesis. Regardless of the chemical nature of the acetylenic monomers and the methods used to polymerise them, polymers with low molecular weights are usually obtained ($\overline{M}_n$ does not exceed 1000–5000). These facts demonstrate the inactivation of the reactive centre during the polymer chain propagation process.

On the one hand, the active centre of the growing chain is linked directly to the conjugated system, so that the reactivity must be evidently influenced by factors which determine the mobility and degree of delocalisation of π electrons. Indeed theoretical calculations based on models involving a conjugated reaction centre[201,212–214,438] confirmed that the delocalisation of the charge or the radical over the conjugation chain with increasing length of the polymeric molecule are the cause of the kinetic deactivation of the active centres. On the other hand, the active radical formed, for example, on dissociation of the triple bond is located in the p_{xy} orbital in the plane perpendicular to that of the conjugated p_z orbitals. In this case the active radical must be appreciably localised in the last unit of the growing chain owing to the weak overlapping of the electronic wave functions and its reactivity should not therefore depend on the chain length.

Thus the mechanism of the delocalisation of the unpaired electron of the growing polymeric radical in radical polymerisation or of the ionic charge in the ionic polymerisation of acetylenes is not self-evident. Therefore, the possibility of the intermolecular inactivation of the reactive centre is postulated together with the intramolecular inactivation[23].

The breakdown of the continuity of the conjugation chain may lead to a growth of the polymer chain which virtually rules out the inactivation of the growing macroradical. Thus the polymerisation of alkylacetylenes containing mobile hydrogen atoms in the α-position relative to the triple bond is accompanied by hydrogen transfer from the alkyl side group to the main chain and the formation of alkylidene side groups[268,305,439,440]:



As a result of the breakdown of the continuity of the conjugated chain, weakly coloured high-molecular-weight polymerisation products are formed.

Long conjugation chains with a coplanar disposition of the C=C bonds are probably unfavourable on thermodynamic and kinetic grounds. The conjugated fragments of macromolecules tend to assume an arrangement relative to one another at an angle in the range $0° < \theta < 90°C$. The macromolecules formed are not planar: they can have different steric conformations in which the exchange interaction of the π electrons diminishes with increase of $\cos^2\theta$. Therefore, in order to estimate the conjugation chain lengths in the macromolecules, the concept of "effective conjugation" or of "block conjugation" has been introduced; it is conventionally expressed in terms of the number of conjugated structural elements having a coplanar arrangement and an electronic absorption or luminescence spectrum analogous to that of the corresponding polymeric homologue as regards the position of the maximum[23,336]. The size of the conjugated block depends on the conditions of the synthesis, but changes little with increase in the length of the macromolecule. The conjugated blocks in polyPA, obtained by thermal polymerisation in bulk at 150°C and in the presence of the $Et_3Al–TiCl_3$ catalytic system in benzene at 70°C, consist of 3–5 and 4–8 units respectively[336,441,442].

The monomeric units in polyPA are combined "head-to-tail"[443–445]. Polyenes obtained under different conditions differ from one another by the position of the substituents both in relation to the double bond and in relation to the chain itself[19,40,224,336,337,446,447]. Four types of chain conformation are possible for polymers of the polyPA type: *trans*-*s*-transoid, *trans*-*s*-cisoid, *cis*-*s*-cisoid, and *cis*-*s*-transoid. For a free rotation of 180° about the single bond, there is a possibility of a transition from the *s*-transoid form to the *s*-cisoid form and converseley. It was found experimentally[336] that polyPA obtained by thermal polymerisation has mainly the *trans*-*s*-cisoid conformation (the angle of rotation about the single bond is $\varphi = 120°C$) with an admixture of the *cis*-structure. The fractions of the polyPA obtained in the presence of $Et_3Al–TiCl_3$ can have the *cis*-*s*-cisoid and *cis*-*s*-transoid conformations ($\varphi = 140–150°$ and $<80°$ respectively). According to calculated data[447], the *cis*-*s*-cisoid conformation ($\varphi = 110°$) is energetically favoured for polyPA. The discrepancy between the calculation and experiment in the last two instances has been attributed by the author[447] to intermolecular interaction. The benzene-soluble polyPA and poly-(α-ethynylnaphthalene) fractions, obtained in the presence of $Fe(DMG)_2.2PyH + Et_3Al$, have the *cis*-*s*-transoid conformation, while block polymerisation of PA and α-ethynylnaphthalene leads to products having the *trans*-transoid structure[337].

Molecules with the *cis*-*s*-cisoid conformation can give rise to close packing of the same type as in molecular crystals. The distances between the molecules are then still so large that intermolecular delocalisation cannot be appreciable. The macromolecules with the *cis*-*s*-transoid conformation are more close packed. Accordingly, Ziegler polyPA is characterised by the presence of crystalline formations (degree of crystallinity about 30%), while thermal polyPA is amorphous[40,448]. Together with the soluble Ziegler polyPA having the *cis*-*s*-transoid conformation and a yellow colour, which has already been considered, a small amount (about 5%) of a red product with a high degree of crystallinity (>70%) and insoluble in organic solvents at room temperature is formed. This product is an assembly of macromolecules with the *cis*-*s*-cisoid structure firmly fixed to the surface of the catalyst. The helical molecular chain contains three monomeric units per repeat period with benzene rings slightly inclined relative to the chain axis. The crystal lattice consists of chains located one above the other without displacement; the packing coefficient is 0.8.[449]

Possibly all the isomeric polyene structures discussed above exist in the helical form and are characterised by a greater (for the *cis*-form) or smaller (for the *trans*-form) packing density. Helical chain conformations impart an ordered structure to the macromolecules, which enables them to be distributed in crystal matrices[337]. The helical structure of the linear conjugated polyhexafluorobut-2-yne is probably responsible for the white colour of this polymer[450].

It has been suggested on the basis of the number and intensity of the diffraction lines and in view of the identity of their periodicities[337] that more ordered packing of the macromolecules is achieved at lower temperatures of the synthesis and that the packing in crystalline matrices depends more on the structure of the main polymer chain than on the nature of the substituent.

The non-stereospecificity of anionic polymerisation noted above can be attributed both to the non-stereospecificity of the addition of the anion to the triple bond and to the isomerisation of the growing anion or the macromolecules when they are isolated and investigated. It is known[224,446,447] that heat treatment or treatment with solvents causes the isomerisation of polyPA. The *cis*–*trans* isomerisation of polyacetylene has been observed on decomposition of catalysts of the Ziegler–Natta type by a mixture of methanol and hydrochloric acid[451] and as a result of the heat generated by a laser source in the recording of Raman spectra[452]. The ratio of the *cis*-transoid and *trans*-transoid structures apparently depends primarily on the temperature of the addition of the first monomeric unit to the catalyst, i.e. on the formation of the complex (XVII). If the transition (XVI) → (XVII) takes place at a low temperature (–78°C), then fully *cis*-transoid poly-(α-ethynylnaphthalene) is formed not only at –78°C but also at a polymerisation temperature of 25°C.[226]

Thus the configuration of the polyene is determined mainly by the composition of the catalyst and the temperature of the synthesis; a *cis*-transoid configuration presupposes the *cis*-dissociation of the triple bond in the polymerisation process. On the other hand, according to electron microscope data, the supermolecular structure of polyenes changes very little with the temperature of the synthesis and is almost independent of the type of the catalyst and its concentration[337,451].

Regardless of the nature of the aromatic substituent, all the polyenes investigated form only globular structures with dimensions up to 300–700 nm. More complex morphological formations in the form of rods or other structures have not been observed even for *cis*-transoid polymers with the highest degree of crystallinity[337,453,454]. The characteristics of the molecular, the supermolecular, and the electronic structures of acetylenic polymers discussed above determine their semiconducting properties[22,112,120,226,455-458].

The dark and photoelectric conductivities of soluble polyvinylenes do not usually exceed $10^{-12}\ \Omega^{-1}\ cm^{-1}$ regardless of the nature of the initial monomer and the polymerisation conditions. The mobility is of an electronic type; as a rule, one is dealing with *p*-type conductivity with a mobility of $10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.[456,459] When a polymer–electron acceptor heterophase system is formed, it is possible to increase greatly the photoconductivity of the system relative to the level of the photoconductivity of both the polymer and the acceptor[460-465]. Not only the corresponding low-molecular-weight compounds but also polymeric compounds, for example the products of the nitration of PA and tolane polymers, can be used as electron acceptors even under the conditions of electrophotography. In the presence of polymeric acceptors, the system exhibits film-forming properties and an improved thermal stability in addition to the enhanced photosensitivity[466,467].

Possibly the increase of photoelectric sensitivity is associated with the spectral sensitisation of the acceptor by the polyene system. Since the spectral sensitisation constitutes the most important procedure for varying the spectral photosensitivity and increasing the integral photosensitivity of silver halides in photography and of zinc oxide in electrophotography, the spectral sensitisation of the photoconductivity of inorganic semiconductors by conjugated polymers is of great interest[468-471]. The electrical conductivity of polymers is defined by the relation[455]:

$$\sigma = q\mu n = q\mu N e^{-E/2kT} \quad ,$$

where q is the elementary charge of the current carriers (electrons), μ the mobility of the carriers, n the number of carriers per unit volume, N the concentration of π electrons, and E the activation energy for conduction (the gap between the valence and conductivity bonds under the conditions of the band mechanism of conduction).

The activation energy is determined mainly by the electron–electron repulsion in the polymer chain; it amounts to 2.5 and 2.4 eV respectively for PA and tolane polymers[472]. The gap may be reduced only when the electron–electron interaction in the polymer chain is weakened, which involves the withdrawal of electrons from the chain under the influence of, for example, electron-accepting side groups[473]. With increase of the degree of conjugation of the cyclic benzene side groups with the main chain, which is achieved by the high-temperature sublimation of the polymer (500°C, 10^{-5} mmHg), the mobility of the holes in the sublimed films of PA and tolane polymers increases from 2×10^{-4} to 0.1 and from 2×10^{-4} to 0.3 $cm^2\ V^{-1}\ s^{-1}$ respectively, while the activation energy for conduction diminishes to 1.4 and 1.3 eV.[472,474,475]

The activation energies for conduction and the mobilities obtained for the sublimed polyphenylvinylene films are probably close to the theoretical limit. Indeed, with decrease of the electron–electron repulsion in the polymer chain under the influence of electron-accepting side group substituents, the concentration of carriers also falls, i.e. the compensation effect comes into force[456].

The mobility of the charge carriers is determined by the intermolecular transitions of these carriers between the conjugated regions. Their low mobility in conjugated polymers in the acetylenic series is due primarily to the low degree of overlapping of the atomic wave functions at the sites corresponding to the breaks in conjugation. Branching and cross-linking in macromolecular chains should therefore lead to a decrease of the activation energy for conduction and to an increase of the mobility of the carriers. Ladder and graphite-like structures can be regarded as limiting cases of the structures of regularly cross-linked polymers.

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The data examined demonstrate an extremely vigorous development in recent years of research on the polymerisation processes of acetylenic compounds. This is associated primarily with efforts directed towards the creation of new organic semiconducting materials. A number of mechanisms have been proposed for the thermal and catalytic polymerisation of acetylenes, which may be regarded as merely hypothetical in view of the contradictory nature or lack of convincing data for the kinetics and mechanisms of the processes. An unambiguous answer to the question of the causes responsible for the deactivation of the growing active centre in the polymerisation of acetylenes has not yet been obtained. There is no doubt that further study of the copolymerisation of alkynes is of interest from both theoretical and practical points of view. We share Myl'nikov's view that "together with the importance of seeking new semiconducting organic polymers there is an urgent necessity for a more detailed investigation of the specific physical structure as solids with a simultaneous development of methods for their purification and for the determination of the impurities"[458]. However, the activation energies for conduction and charge carrier mobilities greater than about 1 eV and about 1 $cm^2 V s^{-1}$ respectively should not probably be expected even for well ordered polyvinylene systems with a linear structure. Studies involving both the synthesis of regular ladder and graphite-like systems and an increase in the photoconductivity of organic semiconductors under the influence of electron acceptors are possibly the most promising in this sense.

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Magnetic Effects in Chemical Reactions

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The Review discusses in what elementary chemical reactions the intrinsic angular momentum of electrons and nuclei is conserved and in what reactions it is not conserved, how weak electron-nuclear magnetic interaction and an external magnetic field influence the conservation of angular momentum and what are the consequences of this effect, and what magnetic effects occur in chemical reactions, as well as the conditions for their development and detection. Conditions are formulated for the non-conservation of the intrinsic angular momentum of electrons and nuclei in chemical reactions. The bibliography contains 36 references.

CONTENTS

I. INTRODUCTION

Chemical processes, i.e. transformations of some molecules into others, are always accompanied by regrouping of nuclei and rearrangement of electron shells. The most important characteristic of such transformations is their energy. In the analysis of chemical processes and the reactivity of reactant species, therefore, it is right to pay maximum attention to the energy aspect. However, it must always be borne in mind that electrons and many nuclei possess intrinsic angular momenta, and the laws of their conservation can exert a marked influence on the direction of chemical reactions and hence on their energetics. Wigner's rule on the conservation of the total electron spin of a reactant system was formulated comparatively long ago, but it is not always satisfied.

The angular momentum of electrons and nuclei is conserved in elementary chemical reactions involving substitution, dissociation, recombination, addition, disproportionation, and electron transfer. If, however, long-lived states, in which transitions are possible between states differing in spin multiplicity, are established in chemical reactions, the angular momentum of electrons and nuclei is not conserved. This leads to the remarkable consequences of magnetic effects in chemical reactions, the most striking of which—chemical polarisation of nuclei, enrichment of magnetic isotopes in chemical reactions, and the effect of a magnetic field on the rates of chemical reactions—are discussed in the present Review.

II. ORIGIN OF MAGNETIC EFFECTS

In most molecules the intrinsic angular momenta (spins) of the electrons balance: i.e. the electrons are coupled. Chemical reactions may take place either without change of spin in the electron-pairs or with uncoupling of the electrons. In the former case the spins in the electron-pairs remain balanced; in the latter case unbalanced individual electron spins appear. The former reactions are classified chemically as heterolytic, and the latter as homolytic or radical.

Magnetic effects must obviously be sought in reactions of the second type, because they involve the production of magnetic moments of electrons, which interact strongly among themselves, with the magnetic moments of the nuclei, and with external magnetic fields. Under certain conditions all these interactions lead to non-conservation of the electronic and the nuclear spin of the reactant system, to the appearance of magnetic effects in chemical reactions. We shall now consider what these effects are and under what conditions they develop.

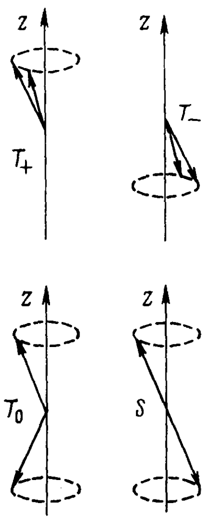


Figure 1. Orientation and precession of electron spins of a radical-pair in an external magnetic field in the z-direction.

In order to understand the origin of magnetic effects in radical reactions it is sufficient to consider as model a simple radical-pair ($HR^{1\cdot}$, $R^{2\cdot}$) in which one radical $HR^{1\cdot}$ contains only one magnetic nucleus (the proton), while the other radical $R^{2\cdot}$ has none. Let the g-factor of the first radical be g_1, and that of the second radical g_2: i.e. the Zeeman energies of the electrons of these radicals in a magnetic field H are $g_1\beta H$ and $g_2\beta H$. We suppose that hyperfine magnetic interaction between electron and proton also occurs in the radical $HR^{1\cdot}$, its energy being am, where $m = \pm\frac{1}{2}$ is the projection of the spin of the proton in the direction of the external magnetic field and a is the electron–proton hyperfine interaction constant. Finally, non-magnetic exchange interaction J occurs between the unpaired electrons of the radical-pair; it forms part of the electrostatic interaction, and is distinguished from the usual Coulombic interaction only in its dependence on the electron spin. Exchange electrostatic forces which depend on the spin of the electrons must be postulated in order to satisfy one of the fundamental principles of quantum mechanics—the Pauli principle.

The spins of the two unpaired electrons in a radical-pair may be oriented in such a way that their vectors must be either added or subtracted, to give a total spin of either unity or zero. Because of the occurrence of exchange interaction the energies of these two states are not the same but differ by the amount J. The state with zero spin is a singlet (S); the state with unit electron spin is termed a triplet (T), since the total electron spin may be oriented in a magnetic field in three different ways with projections of +1, 0, and −1 for the total spin vector in the field direction. These three substates T_+, T_0, and T_- differ in their Zeeman energies, which are respectively $g\beta H$, 0, and $-g\beta H$, where $g = \frac{1}{2}(g_1 + g_2)$. The scheme of orientation of electron spins in a radical-pair is shown in Fig. 1, and the energy levels of the states corresponding to these orientations are indicated in Fig. 2.

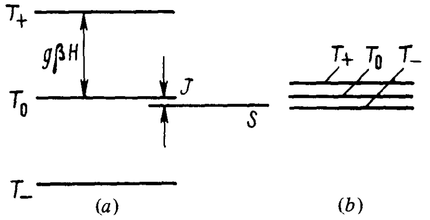


Figure 2. Energy levels of a radical-pair in a magnetic field: a) strong; b) weak.

We shall now suppose that the radical-pair is in a triplet state. Such a pair must undergo a transition to a singlet state before it is able to recombine to give the reaction product. Thus the probability of recombination (or disproportionation), with the formation of molecular products having zero total electron spin, is proportional to the probability of triplet–singlet transition. The latter probability is proportional to the square of the matrix element calculated from the spin wave functions of state S and T and the spin Hamiltonian $\mathscr{H}$ of the pair:

$$p_{T\text{-}S} \sim |\langle T|\mathscr{H}|S\rangle|^2. \tag{1}$$

The Hamiltonian $\mathscr{H}$ defines the interactions of electrons and nuclei in the pair:

$$\mathscr{H} = \beta H(g_1S_1 + g_2S_2) - J(^1/_2 + 2S_1S_2) + aIS_1\,, \tag{2}$$

where the first term represents the Zeeman interaction of the electrons, the second term the exchange interaction, the third term the hyperfine interaction between electron and proton in the $HR^{1}\cdot$ radical, S_1 and S_2 are the spins of the first and second electrons, and I is the spin of the proton. The matrix element for the transition T_0–S is

$$\langle T_0|\mathcal{H}|S\rangle = {}^1/_2(\Delta g\beta H + am) \tag{3}$$

in which $\Delta g = g_1 - g_2$ and $m = \pm\frac{1}{2}$ (for the proton). The matrix elements for transition from states T_+ and T_- to state S are

$$\langle T_+(-{}^1/_2)|\mathcal{H}|S(+{}^1/_2)\rangle = -({}^1/_8)^{{}^1/_2}a, \tag{4}$$

$$\langle T_-(+{}^1/_2)|\mathcal{H}|S(-{}^1/_2)\rangle = ({}^1/_8)^{{}^1/_2}a. \tag{5}$$

(The procedure for calculating such matrix elements will be found in greater detail in Ref. 1).

The expressions $(\pm\frac{1}{2})$ in Eqns. (4) and (5) denote the projections of the spin of the proton; triplet–singlet transitions from states T_+ and T_- are obviously allowed only in the presence of hyperfine electron–nuclear interaction, and are necessarily accompanied by reorientation of the nuclear spin: $T_+(-\frac{1}{2}) \to S(+\frac{1}{2})$ and $T_-(\frac{1}{2}) \to S(-\frac{1}{2})$. Thus it is important for transitions from T_+ and T_- states to the S state that hyperfine interaction should involve a single electron–nucleus system; the change in electron spin accompanying the triplet–singlet transition will then be balanced by a change in the nuclear spin.

Thus a triplet–singlet transition is accompanied by a change in the total electron spin and is therefore forbidden. However, if the unpaired electrons attached to the components of a radical-pair differ in their Zeeman energy and if hyperfine interaction links electronic and nuclear spin systems, the prohibition on such a transition is partly removed. This partial elimination of spin prohibitions is the cause of the magnetic effects.

Before analysing magnetic effects we note that the mean exchange interaction is small in radical-pairs in a liquid, and the exchange energy can be neglected (proofs of this statement will be given later). Therefore in strong magnetic fields, when the Zeeman energy $g\beta H$ is large, the T_+ and T_- levels are remote from S, and the main contribution to triplet–singlet mixing is made by transitions between contiguous T_0 and S levels. In weak magnetic fields $g\beta H$ is small, all three levels T_+, T_0, and T_- are situated close to the level of the singlet state, and transitions from all the triplet substates are important for triplet–singlet mixing (Fig. 2). We shall now enumerate the principal magnetic effects.

(i) It follows from Eqns. (3)–(5) that the probability of triplet–singlet transitions and hence the probability of reaction depend on the nuclear spin of the radical. As a consequence the recombination products are enriched (or impoverished) in nuclear spins of a certain orientation: i.e. a non-equilibrium population of Zeeman nuclear levels is produced in the reaction products. Such non-equilibrium population or pumping of Zeeman levels results in a non-equilibrium orientation or polarisation of nuclei in the molecules generated from the radical-pairs. This phenomenon of chemically induced magnetic polarisation of nuclei was discovered by Fischer and Bargon and independently by Ward and Lawler in 1967, and has become widely known[2,3].

(ii) It follows also from Eqns. (3)–(5) that the probability of recombination depends on the hyperfine electron–nuclear interaction energy. Isotope effects should be observed in the rates of recombination of the components of radical-pairs, since the nuclei of isotopes possess different magnetic moments and hence have different hyperfine interaction constants.

(iii) The dependence of the probability of recombination of radicals on the hyperfine interaction energy (or on the magnetic moment of the nuclei) makes possible the selection and enrichment of magnetic isotopes in chemical reactions. This effect is purely magnetic in origin, so that a method of isotope enrichment that can be based on it differs fundamentally from other methods (e.g. the selective dissociation of chemical bonds by laser illumination, which utilises the isotope effect on vibration frequencies due to the difference in mass between isotopes[4]).

(iv) Another consequence of Eqn. (3) is that the probability of recombination of the radicals forming a pair depends on the strength of the external magnetic field (provided that the radicals have different g-factors, i.e. that $\Delta g \neq 0$). This gives rise to quite definite and soundly based ideas on the causes and the physical mechanisms of the influence of an external magnetic field on the direction and the rates of chemical reactions. In the case of radical reactions a magnetic field affects the rate of triplet–singlet conversion and changes the probability of recombination. This mechanism is readily generalised to cover any reactions involving species in higher spin states, with a larger number of unpaired electrons (e.g. iron and copper ions, molecular oxygen, etc.). In such cases the magnetic field also influences the probabilities of intersystem transitions between states differing in spin multiplicity (doublets, triplets, quartets, quintets, etc.) in reactant-pairs, and consequently changes the probabilities of chemical reactions.

Each of these four effects will be discussed further. Before proceeding to their detailed analysis, however, we can usefully extend the key equations (3)–(5) to cover any pair of radicals with any number of nuclei. The spin Hamiltonian of such a generalised pair is

$$\mathcal{H} = \beta H(g_1S_1 + g_2S_2) - J({}^1/_2 + 2S_1S_2) + \sum_i a_iS_1I_i + \sum_j a_jS_2I_j \quad , \tag{6}$$

where I_i is the spin of the ith type of nucleus in the first radical, I_j is the spin of the jth type of nucleus in the second radical, and a_i and a_j are the corresponding hyperfine interaction constants. The matrix element of triplet–singlet mixing for a transition from the T_0 state is

$$\langle T_0|\mathcal{H}|S\rangle = {}^1/_2\left(\Delta g\beta H + \sum_i a_im_i^a - \sum_j a_jm_j^b\right) , \tag{7}$$

where the m_i^a are the projections of nuclear spins of the ith kind in the first radical, the m_j^b are the projections of nuclear spins of the jth kind in the second radical, and the summation covers all nuclei in both radicals. The three terms in Eqn. (7) are respectively the difference in the Zeeman energies of the electrons, the sum of the hyperfine interaction energies in the first radical, and the corresponding sum in the second radical of the pair. The matrix elements of triplet–singlet mixing from states T_+ and T_- are

$$\langle T_+, m_i - 1|\mathcal{H}|S, m_i\rangle = -({}^1/_8)^{{}^1/_2}a_i[I_i(I_i + 1) - m_i(m_i - 1)] , \tag{8}$$

$$\langle T_-, m_i + 1|\mathcal{H}|S, m_i\rangle = ({}^1/_8)^{{}^1/_2}a_i[I_i(I_i + 1) - m_i(m_i + 1)] . \tag{9}$$

As with the model one-proton radical-pair (Eqns. 4 and 5), triplet–singlet transitions from states T_+ and T_- are obviously allowed only in the presence of hyperfine electron–nuclear interaction, and are accompanied by reorientation of the nuclear spin of the ith kind: in a T -S transition the nuclear spin increases $(m_i - 1 \to m_i)$; in a T_--S transition the nuclear spin diminishes $(m + 1 \to m_i)$.

The probabilities of all these transitions are proportional to the squares of the matrix elements (7)–(9). It is readily seen that Eqns. (3)–(5) are particular cases of the general equations (7)–(9): they are obtained with $m_i = \pm\frac{1}{2}$, i.e. for a one-proton radical-pair.

III. CHEMICAL POLARISATION OF NUCLEI

1. Physical Mechanisms of the Chemical Polarisation of Nuclei

The chemical polarisation of nuclei has acquired great popularity, with accounts of its theory and chemical applications in several books and reviews[2,3,5-7]. For this reason only a brief discussion will appear here of the evolution of ideas in this field, of the current state of the theory, and of chemical applications of the phenomenon.

We shall first discuss the mechanisms by which nuclear polarisation is produced. As noted above, the main contribution to triplet–singlet conversion of a radical pair is made in strong magnetic fields by transitions from the T_0 state. Equation (3) shows that, if $\Delta g > 0$ and $a > 0$, the probability of triplet–singlet transition is greater in a radical-pair having $m = +\frac{1}{2}$ than in a pair having $m = -\frac{1}{2}$. This means that pairs having a proton oriented in the direction of the field undergo triplet–singlet conversion more rapidly and hence recombine more rapidly: i.e. the products of recombination (or disproportionation) are enriched with positively polarised nuclei. On the other hand, radicals that have avoided recombination in the radical-pair and have escaped into space contain an excess of protons oriented against the field, and these radicals confer on their conversion products a negative nuclear polarisation. Thus T_0–S transitions in radical-pairs involve a selection of radicals according to their nuclear spins: chemical reactions lead to selection, to a sorting of radicals (and hence of molecules produced from them) according to their nuclear-spin states.

It is readily seen that, if the sign of Δg or a is changed in Eqn. (3), the sign of the nuclear polarisation also changes. For the same reason the sign of the polarisation is reversed if the precursor of the molecules is not a triplet but a singlet pair, when the reverse singlet–triplet conversion of the pair takes place. It is easy to predict from Eqn. (3) the sign of the chemical polarisation of nuclei as a function of those of Δg and a and the spin state of the radical-pair. Kaptein[8] suggested for this the convenient form

$$\Gamma = \mu\varepsilon\,\Delta g a \tag{10}$$

known as Kaptein's rule, in which $\mu = +1$ if the precursor of the molecule is a triplet pair, $\mu = -1$ if the precursor is a singlet pair, $\epsilon = +1$ for a product of recombination or disproportionation, $\epsilon = -1$ for conversion products of radicals outside a pair, Δg and a determine the signs of these quantities $\Gamma > 0$ corresponds to positive polarisation (A, absorption in the nuclear magnetic resonance spectra by molecules having polarised nuclei), and $\Gamma < 0$ corresponds to negative polarisation (E, emission in the n.m.r. spectra).

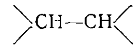
Integral polarisation of a given group of nuclei arises only when $\Delta g \neq 0$. If $\Delta g = 0$, an unusual type of polarisation often appears, which is characteristic of groups of nuclei having spin–spin interaction. In this case the components of the spin multiplet, appearing at high and low fields, correspond to polarisation of different signs; this type of polarisation is termed the multiplet effect or multiplet polarisation.

It is easy to show that multiplet polarisation is produced by the same mechanism as is integral polarisation, i.e. by the dependence of the rate of triplet–singlet transitions in radical-pairs on the nuclear spin of the radicals. Let us consider a simple pair of radicals

each of which contains one proton; the pair is initially in a triplet state, and also has $\Delta g = 0$. Equation (7) then simplifies to

$$\langle T_0|\mathscr{H}|S\rangle = {}^1/_2\,(a_1m^a - a_2m^b). \tag{11}$$

If $a_1 < 0$ and $a_2 < 0$, pairs having proton orientations $m^a = \frac{1}{2}$, $m^b = -\frac{1}{2}$ and $m^a = -\frac{1}{2}$, $m^b = \frac{1}{2}$ will obviously pass into the singlet state more rapidly, so that



molecules, in which the two protons have opposite spin orientations, will predominate in the product of recombination. The scheme of population of nuclear-spin levels in such a molecule is shown in Fig. 3, where the arrows denote n.m.r. transitions, which lead to a multiplet effect AE (the components of the spin multiplet correspond to positive polarisation at low field, and to negative polarisation at high field).

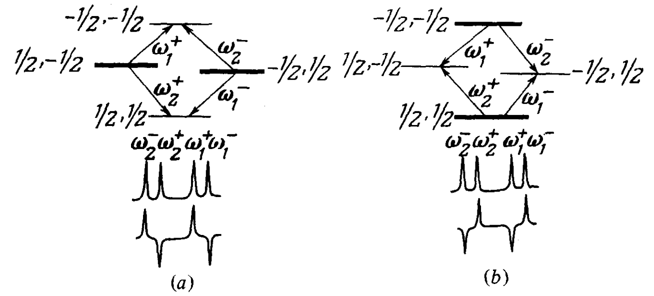


Figure 3. Multiplet effect in a fragment $>$CH–CH$<$ of a molecule generated from a triplet pair: a) AE; b) EA.

It is readily seen from Eqn. (11) also that, if the sign of one of the hyperfine interaction constants is changed (e.g. $a_1 > 0$, $a_2 < 0$), the populations of the levels and the sign of the multiplet effect are changed (Fig. 3b). These properties are readily predicted from Eqn. (7) for any case. A convenient formula for such prediction was proposed by Kaptein[8]:

$$\Gamma_{\rm ME} = \mu\varepsilon a_i a_j J_{nn}\sigma_{ij}\,, \tag{12}$$

where μ and ϵ have the same significance as in (10), a_i and a_j are hyperfine interaction constants, J_{nn} is the spin–spin interaction constant of the nuclei in the molecule (only the signs of these quantities are important here), $\sigma_{ij} = 1$ if the nuclei i and j are present in the same radical of the pair, and $\sigma_{ij} = -1$ if they belong to different radicals. The multiplet effect has the sign of EA when $\Gamma_{ME} > 0$, and that of AE when $\Gamma_{ME} < 0$.

Thus Eqns. (3) and (7) define the signs of the integral and multiplet polarisation produced in strong fields when transitions from the T_0 state are mainly responsible for the triplet–singlet conversion of the pair. These equations have been obtained by quantum-mechanical calculation. It is not difficult to show that the same result—the dependence of the rate of triplet–singlet conversion on the nuclear spin—can be obtained from classical physics.

We shall demonstrate this on the model one-proton pair ($HR^{1}\cdot$, $R^{2}\cdot$). The orientations of the electron spin vectors of the pair are indicated in Fig. 1. These vectors are known to precess about the z-axis (the direction of the external magnetic field). In order that the transition $T_0 \rightarrow S$ should occur the vectors must be "unwound" relative to each other by 180°: i.e. it is necessary that the difference of phase in the precession of the two electrons should be π. The frequency of precession of the first electron is $g_1\beta H \pm \frac{1}{2}a$ depending on whether the spin of the proton is directed with or against the field. That of the second electron is $g_2\beta H$. The corresponding frequency differences between the two electrons are $\Delta g\beta H \pm \frac{1}{2}a$. In order that the transition $T_0 \rightarrow S$ should take place it is necessary that

$$(\Delta g\beta H + {}^{1}/{}_{2}a)\, t_\alpha = \pi \ \text{(proton with the field)}$$
$$(\Delta g\beta H - {}^{1}/{}_{2}a)\, t_\beta = \pi \ \text{(proton against the field)}\ ,$$

where t_α and t_β are the transition times in a pair having nuclear spins α and β. If Δg and a have the same sign, we obviously obtain $t_\alpha < t_\beta$: i.e. radical-pairs in which the proton is oriented in the direction of the field pass into the singlet state and recombine more rapidly. The triplet–singlet conversion of pairs in which the proton is oriented against the field lags behind, and such pairs have a greater chance of dissociating. The result is the selection of radicals according to nuclear-spin states—in agreement with the quantum-mechanical equations (3) and (7).

From the classical picture of a triplet–singlet conversion it is not difficult to estimate the conversion time

$$t_{T_0-S} \simeq (\Delta g\beta H + am)^{-1}$$

for a one-proton pair, or in general

$$t_{T_0-S} \simeq \Big(\Delta g\beta H + \sum_i a_i m_i^a - \sum_j a_j m_j^b\Big)^{-1} \quad . \tag{13}$$

With the usual values of the g-factors and the hyperfine interaction constants in organic radicals this time amounts to $\sim 10^{-9}$–10^{-8} s.

In weak magnetic fields the contribution by T_0–S transitions to the integral polarisation becomes negligible, because the difference $\Delta g\beta H$ between the Zeeman energies is small in weak fields. This is accompanied by increased contributions to the polarisation by T_+–S and T_-–S transitions, which entail reorientation of nuclear spins—in conformity with Eqns. (4), (5) and (8), (9).

In contrast to T_0–S transitions, in which the z-component (projection) of the total electron spin remains unchanged, so that the nuclei do not change their orientation, T_+–S and T_-–S transition are accompanied by a change in the z-component of the electron spin and reorientation of the nuclear spins. In fact, T_0–S transitions in radical-pairs involve merely a sorting-out of nuclear spins according to orientation, whereas in T_+–S transitions a fresh orientation of the nuclei is established. For this reason the chemically induced polarisation of nuclei shows considerable differences between weak and strong magnetic fields (for greater detail see Refs. 2, 3, 5, and 6).

2. Main Stages in the Development of the Chemical Polarisation of Nuclei

The discovery of the phenomenon itself must be regarded as the first stage in the development of the chemical polarisation of nuclei; as already stated above, it was made simultaneously and independently by two groups of investigators. It is surprising that this occurred accidentally in both cases: the actual investigations in which the new phenomenon was discovered were on an extremely trivial plane, which is quite instructive from a methodological point of view.

The first attempt to explain the phenomenon in terms of the Overhauser effect was unsuccessful. The four chief experimental criteria of the chemical polarisation of nuclei—the dependence of polarisation on the type of chemical reaction, establishment of the phenomenon in the products of cage recombination, unusually large polarisation coefficients, and finally the multiplet effect—do not fit into the framework of the Overhauser effect.

The second stage began in 1969, when Kaptein and Oosterhoff[9] and independently Closs[10] almost simultaneously suggested that chemical polarisation of nuclei appeared in radical-pairs on triplet–singlet transitions, whose probability depends on the nuclear spin. This idea and the qualitative explanation of the phenomenon based on it have been examined above. We shall now consider the quantitative theory of the chemical polarisation of nuclei.

The probability that a molecule will be formed in the nuclear spin state ab is the integral of the product of three probabilities:

$$P_{ab} = \int_0^\infty \varepsilon\, |c_{S,ab}(t)|^2\, \mathrm{f}(t)\, \mathrm{d}t \quad . \tag{14}$$

Here $|c_{S,ab}(t)|^2$ is the probability that the pair will pass into a singlet state by time t (if the initial state of the pair were a triplet) or remain in the singlet state by this time (if the initial state of the pair were a singlet), i.e. the probability that the pair will be by time t in a singlet state and will be ready for recombination. The function $\mathrm{f}(t)$ represents the lifetime distribution of the pairs: $\mathrm{f}(t)dt$ is the probability that the pair will survive to time t and be destroyed by time $t + dt$. The coefficient ϵ denotes the probability that a pair that has survived from time t and is by then in a singlet state, i.e. completely prepared for recombination, will finally recombine (or disporportionate).

The quantity $|c_{S,ab}(t)|^2$ is obtained by solving the time-dependent Schrödinger equation with the time-independent Hamiltonian of the pair (6). It is supposed that only the spin functions of the pair vary with time, these being produced by the superposition of the wave functions of singlet and triplet states. The quantity $c_{S,ab}(t)$ is essentially a coefficient of the singlet component of the spin function of the pair, and its square a contaminant of the singlet state. If the pair were initially in a triplet state, in strong magnetic fields we have

$$|c^T_{S,ab}(t)|^2 = (\mathscr{H}^2_{ab}/D^2_{ab}) \sin^2 D_{ab}t, \tag{15}$$

where

$$\mathscr{H}_{ab} = \langle T_0 | \mathscr{H} | S \rangle = \frac{1}{2}\Big(\Delta g\beta H + \sum_i a_i m_i^a - \sum_j a_j m_j^b\Big) \tag{16}$$

is a matrix element of T_0–S mixing (Eqn. 7) and

$$D_{ab} = (\mathscr{H}_{ab}^2 + J^2)^{1/2} \; . \tag{17}$$

If the initial state of the pair is a singlet, then

$$|c_{S,ab}^S(t)|^2 = \frac{1}{n} - \frac{\mathscr{H}_{ab}^2}{D_{ab}^2} \sin^2 D_{ab} \; . \tag{18}$$

The subscript ab denotes the nuclear spin state of the pair, where a and b represent the sets of nuclear spins of the first and second radicals respectively and n is the total number of nuclear spin states of the radical-pair (and of the molecule generated from the pair). Equation (18) is obtained from the condition for normalisation: the total probability of finding the pair in the nuclear spin state ab is $1/n$, independently of whether the pair exists at the given moment in a singlet or a triplet state.

The theory was originally based on a static model of the pair, in which

$$\mathrm{f}(t) = \frac{1}{\tau} \exp(-t/\tau), \tag{19}$$

where τ is the lifetime of the radical-pair. From Eqn. (14) together with (15) and (19) we find that the probability of formation of a molecule in the nuclear spin state ab from a triplet pair is in this case

$$P_{ab} = 2\varepsilon\mathscr{H}_{ab}^2\tau^2/(1 + 4D_{ab}^2\tau^2). \tag{20}$$

This quantity is essentially the population of the state ab in the molecule: the coefficient of nuclear polarisation in the transition ab–$a'b'$ is the difference between those of states ab and $a'b'$ related to the equilibrium, Boltzmann difference between the populations of these states. Similarly, it is easy to calculate the populations in molecules generated from singlet pairs, by substituting Eqns. (18) and (19) in (14), a variant known as the Closs–Kaptein–Oosterhoff theory.

With reasonable lifetimes $\tau \simeq 10^{-12}$–10^{-11} s for the pairs this theory gave calculated polarisations that were too small. Experimental values far exceeded those predicted theoretically (examples of calculations will be found in Ref. 4). The reason for such a discrepancy is obvious: as shown above (§III, 1) the duration of a triplet–singlet transition is 10^{-9}–10^{-8} s, in comparison with which the lifetime of a pair is too short and insufficient for triplet–singlet conversion of the pair and the accompanying selection of radicals according to nuclear spins.

The third stage in the development of the theory of the chemical polarisation of nuclei was initiated by the publications of Adrian[11–13], who suggested a dynamic model of a radical-pair, in which the radicals are able to diffuse into space, diverge, and again return to the initial pair after completing diffusion migrations. The probability of return gradually diminishes with increase in length of the diffusion path, so that the probability of the radicals meeting again decreases with increase in this length and hence in the duration of diffusion. However, a longer path entails a longer time of triplet–singlet evolution and hence greater efficiency of selection of radicals according to nuclear spins. In the dynamic model

$$\mathrm{f}(t) = mt^{-3/2} \tag{21}$$

a function used by Noyes[14] to interpret the kinetics of liquid-phase reactions. It has recently received direct experimental support from flash photolysis in the picosecond range[15].

From Eqns. (21) and (14) we find that the population of the nuclear spin state ab in a molecule generated from a triplet pair is

$$P_{ab}^T = \pi^{1/2}\varepsilon m (\mathscr{H}_{ab}/D_{ab})^2 |D_{ab}|^{1/2} \; . \tag{22}$$

In order to calculate the population in a molecule generated from a singlet pair we must bear in mind that the majority of the pairs recombine immediately after formation (primary recombination), and radicals separate only from the remaining pairs, diffusing away, returning, and again meeting (secondary recombination). Only pairs that have undergone secondary recombination are subject to singlet–triplet evolution, and only in them is nuclear polarisation produced. For the population of the nuclear spin state ab in a molecule generated from a singlet pair we can therefore write

$$P_{ab}^S = \frac{\alpha}{n} + (1-\alpha)\int_0^\infty \varepsilon |c_{S,ab}^S(t)|^2 \mathrm{f}(t)\,\mathrm{d}t \; . \tag{23}$$

The first term in (23) represents the probability of primary recombination, and the second term the population produced in pairs that have undergone secondary recombination. It is noteworthy that α and ϵ are similar in physical meaning and probably in magnitude (~0.5–0.8); the slight difference between them is that α relates to a primary pair, in which the radicals may be separated by foreign molecules (e.g. in the decomposition of acyl peroxides $R^1CO.O.O.CO.R^2$ a CO_2 molecule separates the pair of radicals $R^1\cdot$ and $R^2COO\cdot$), whereas ϵ defines the probability of recombination in a contact pair. Substituting (18) in (23), we obtain the population

$$P_{ab}^S = \frac{\alpha}{n} + (1-\alpha)\left[\frac{1}{n}\int_0^\infty \varepsilon\,\mathrm{f}(t)\,\mathrm{d}t - \pi^{1/2}\varepsilon m (\mathscr{H}_{ab}/D_{ab})^2 |D_{ab}|^{1/2}\right] . \tag{24}$$

The first two terms are not well defined, but this has no significance, since only the difference between the populations is important for calculating the polarisation, and these terms do not enter into this difference.

If a molecule is produced by chance encounters of independently generated radicals, its precursor is a pair whose initial state may equally probably have been singlet or triplet T_0 (such pairs are said to be uncorrelated). Some of the singlet pairs undergo primary recombination, and the remainder singlet–triplet evolution and secondary recombination. All those pairs that have been in a T_0 state undergo the reverse, triplet–singlet evolution. The nuclear polarisation produced in these pairs is the net result of such complicated evolution and can be calculated without difficulty[3] (for uncorrelated pairs $\epsilon = \alpha$).

The introduction of a dynamic model of a pair into the chemical polarisation of nuclei immediately solved several theoretical difficulties. Quantitative agreement between theory and experiment improved markedly. The physically unreal model of a static pair, in which the radicals were fixed at a definite distance for an unnaturally long time, became unnecessary. Quantitative calculations were simplified, for it became clear that the greatest contribution to the polarisation was made by long diffusion paths with the long time required for successful T–S evolution. It is on such paths that the radicals diverge far apart, so that the exchange energy of the electrons J can be neglected with good approximation. It is easily seen that Eqns. (22) and (24) then simplify to

$$P_{ab}^T = \pi^{1/2}\varepsilon m |\mathscr{H}_{ab}|^{1/2} \; , \tag{25}$$

$$P_{ab}^S = \frac{\alpha}{n} + \frac{(1-\alpha)}{n}\int_0^\infty \varepsilon\,\mathrm{f}(t)\,\mathrm{d}t - (1-\alpha)P_{ab}^T \; . \tag{26}$$

It immediately became possible to dispense with (which was entirely justified physically) a fairly inconvenient and indeterminate theoretical parameter.

Even with a dynamic model of the pair, however, difficulties remained in the theory of the chemical polarisation of nuclei. Firstly, the function f(t) does not take into account the finite lifetime of the radicals (more correctly, it assumes that the radicals exist for an indefinite time). Secondly, theory does not reproduce the dependence of the polarisation on the magnetic interaction energy: it predicts that the polarisation will be proportional to $|\mathcal{H}_{ab}|^{\frac{1}{2}}$—see Eqns. (25) and (26)—whereas proportionality both to $|\mathcal{H}_{ab}|^{\frac{1}{2}}$ and to $\mathcal{H}^2_{ab}$ has been found experimentally. The overcoming of these difficulties constituted the fourth stage in the development of the chemical polarisation of nuclei, which characterises the current state of the theory.

3. Current State of the Theory

In order to correct defects in the dynamic model of a pair the modified function

$$\mathrm{f}(t) = m t^{-3/2} \exp(-t/\tau) \tag{27}$$

has been suggested[16,17], where τ is the characteristic lifetime of the radical, the time of its conversion into another radical (by decomposition or substitution), as a result of which the initial pair disappears and is replaced by a new pair. The function f(t) in the form (27) describes an exponential distribution of diffusion paths with respect to length (and duration).

Substituting (27) in (14) and calculating the difference between the populations of the nuclear spin states ab and $a'b'$ in a molecule generated from a triplet pair, we obtain

$$\begin{aligned} P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m \Big\{ &[(2\mathcal{H}_{ab})^2 + \tau^{-2}]^{1/4} \cos\frac{\arctan(2\mathcal{H}_{ab}\tau)}{2} - \\ &- [(2\mathcal{H}_{a'b'})^2 + \tau^{-2}]^{1/4} \cos\frac{\arctan(2\mathcal{H}_{a'b'}\tau)}{2}\Big\} = X(\tau) \ . \end{aligned} \tag{28}$$

It can readily be shown that in the two limiting cases—short-lived radicals ($\tau \ll \mathcal{H}^{-1}_{ab}, \mathcal{H}^{-1}_{a'b'}$) and long-lived radicals ($\tau \gg \mathcal{H}^{-1}_{ab}, \mathcal{H}^{-1}_{a'b'}$)—Eqn. (28) leads to the formulae

$$P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m \tau^{3/2} (\mathcal{H}^2_{ab} - \mathcal{H}^2_{a'b'}) \ , \tag{29}$$

$$P^T_{ab} - P^T_{a'b'} = \pi^{1/2}\varepsilon m (|\mathcal{H}_{ab}|^{1/2} - |\mathcal{H}_{a'b'}|^{1/2}) \ . \tag{30}$$

Thus with short-lived radicals the polarisation is proportional to the difference between the squares of the matrix elements of triplet–singlet mixing (as in the static model). With long-lived radicals the polarisation is proportional to the difference between the square roots of the matrix elements (as in Adrian's dynamic model). Hence Eqn. (28) is a general expression for the difference in populations, from which the equations of the Closs–Kaptein–Oosterhoff and Adrian theories are obtained as particular, asymptotic solutions.

Nor is it difficult to deduce expressions for the difference between the populations of nuclear spin states in a molecule generated from a singlet pair or from an uncorrelated pair:

$$P^S_{ab} - P^S_{a'b'} = -(1-\alpha) X(\tau) \tag{31}$$

$$P^U_{ab} - P^U_{a'b'} = {}^1/_2 \alpha X(\tau) \ , \tag{32}$$

where $X(\tau)$ has been given by Eqn. (28). It follows also from these equations that the polarisation of molecules generated from triplet and uncorrelated pairs has the same sign but is opposite to the polarisation of molecules from a singlet pair (in agreement with earlier, qualitative predictions). The polarisations from these pairs are in the proportions $1 : \frac{1}{2}\alpha : -(1-\alpha)$ and depend on the probability of primary recombination; in particular, when $\alpha = 0.8$ the proportions are $1 : 0.4 : -0.2$.

An important stage in the development of the chemical polarisation of nuclei and its application to chemistry and chemical kinetics was the establishment of a kinetic theory linking the kinetics of the polarisation with that of chemical reactions[4,18]. The principal equation is

$$\frac{\mathrm{d}I}{\mathrm{d}t} = E\frac{\mathrm{d}I_0}{\mathrm{d}t} - \beta(I - I_0), \tag{33}$$

where I is the nuclear magnetisation (or n.m.r. signal) during the reaction and I_0 is the corresponding equilibrium magnetisation (or equilibrium n.m.r. signal). The first term defines the rate of chemical pumping, the rate of establishment of polarisation; while the second term is the rate of its destruction, the rate of relaxation of the non-equilibrium magnetisation to its equilibrium value $\beta = T_{1n}^{-1}$, in which T_{1n} is the nuclear relaxation time in the molecule. Solutions describing the kinetics of chemical reactions occurring under various régimes were obtained from Eqn. (33).[4] The kinetic parameters of the reaction, the nuclear relaxation times, and the polarisation coefficient E could be obtained by comparison with experiment.

This last parameter is of especial interest for the theory; it shows the factor by which the non-equilibrium nuclear polarisation of a molecule at the instant of its generation from a radical-pair exceeds its equilibrium, Boltzmann polarisation (in particular, $E = 1$ for molecules having the equilibrium polarisation). In other words, the coefficient of nuclear polarisation is the ratio of the non-equilibrium difference in population of nuclear spin states to its equilibrium value:

$$E = \langle P_{ab} - P_{a'b'} \rangle / (P^0_{ab} - P^0_{a'b'}) \ , \tag{34}$$

where

$$P^0_{ab} - P^0_{a'b'} = p^0_n = \tan\mathrm{h}\,\frac{\hbar\gamma_n H}{2kT} \ .$$

The coefficient E is determined experimentally from the kinetics of the chemical polarisation of nuclei and applies to a molecule, a molecular group, or a certain nuclear spin transition between states ab and $a'b'$ in the molecule. Populations are calculated and normalised per single radical-pair. In order to determine the polarisation parameters from experimental polarisation coefficients E, therefore, the relation between the coefficient and the populations of nuclear spin states must be established.

Molecules for which the polarisation coefficient has been determined experimentally are generated in various nuclear spin states, with various population differences; some of them contain no excess polarisation at all (e.g. those formed from singlet pairs in primary recombination). For this reason the experimental polarisation coefficient for the ab–$a'b'$ transition is an average value:

$$E_{ab-a'b'} = \sum_i E_i p_i, \tag{35}$$

where E_i is the partial polarisation coefficient for the ith molecular species and p_i the fractional content of these molecules. For example, the mean polarisation coefficient of the transition for a molecule generated from a triplet pair is

$$E^T_{ab-a'b'} = \frac{P_{ab} - P_{a'b'}}{P^0_{ab} - P^0_{a'b'}} \cdot \frac{P_{ab} + P_{a'b'}}{\sum\limits_{ab} P_{ab}} + \frac{P^0_{ab} - P^0_{a'b'}}{P^0_{ab} - P^0_{a'b'}} \left(1 - \frac{P_{ab} + P_{a'b'}}{\sum\limits_{ab} P_{ab}}\right). \tag{36}$$

The first term gives the contribution to the total polarisation by those molecules that have been generated in the nuclear spin states *ab* and *a'b'*; all the remaining molecules are generated in other nuclear spin states, so that they contribute the equilibrium polarisation to the given transition *ab*–*a'b'*. The first of the multipliers in the terms in (36) correspond to the partial polarisation coefficients of these molecules, and the second of the multipliers to their partial fraction; $\sum_{ab} P_{ab}$ is the total probability of generation of a molecule summed over all nuclear spin states. The second term is obviously negligibly small, so that from (28) we have

$$E^{T}_{ab-a'b'} = \frac{X(\tau)}{p^{0}_{n}} \Phi^{T}, \tag{37}$$

where

$$\Phi^{T} = \frac{(P_{ab} + P_{a'b'})}{\sum\limits_{ab} P_{ab}}$$

is the fraction of molecules that have been generated in states *ab* and *a'b'*. It can easily be deduced that e.g. for a pair with one proton $\Phi^{T} \simeq 1$, and for a two-proton pair $\Phi^{T} \simeq \frac{1}{2}$. In general, for a polyproton system containing *m* protons in the pair $\Phi^{T} \simeq 2^{1-m}$. Values of P_{ab} and hence of Φ^{T} can in principle be calculated for any specific system.

Similarly, formula (35) can readily be used to express the experimental polarisation coefficient for the *ab*–*a'b'* transition in a molecule generated from a singlet pair:

$$E^{S}_{ab-a'b'} = -\frac{(1-\alpha) X(\tau)}{p^{0}_{n}} \Phi^{S}, \tag{38}$$

where

$$\Phi^{S} = \frac{P^{S}_{ab} + P^{S}_{a'b'}}{\sum\limits_{ab} P^{S}_{ab}}$$

$$\sum_{ab} P^{S}_{ab} = \alpha + (1-\alpha)\int\limits_{0}^{\infty} \varepsilon f(t)\,dt - (1-\alpha)\sum_{ab} P^{T}_{ab}\ .$$

The exact expression for Φ^{S} is more cumbersome than that obtained with a triplet pair; however, it can be accepted approximately that $\Phi^{S} \simeq 2/n$. If the molecule contains *m* protons, for example, we have $\Phi^{S} \simeq 2^{1-m}$. In the same way expressions can be obtained for the polarisation coefficient of a molecule from an uncorrelated pair.

The meaning and purpose of these equations lie in the theoretical calculation (in terms of population differences) of nuclear polarisation coefficients and hence, from a comparison of the results with experimental values, determination of the parameters of chemical nuclear polarisation (magnetic parameters of the pair, lifetimes of the radicals). This approach to a quantitative analysis of the phenomenon has several advantages over the simulation of n.m.r. spectra of molecules with polarised nuclei. The chief advantage is that we can disregard relaxation effects in the molecules and their distorting effects on the populations of levels and the chemical nuclear polarisation spectra; the difficulties entailed in allowing for relaxation in the simulation of the spectra led to several errors in the analysis of the chemical polarisation of nuclei (for further details see Ref. 4).

All the theoretical approaches discussed here are essentially semi-empirical, since they involve two hypothesis. Firstly, it is assumed that the spin Hamiltonian of a radical-pair is independent of time, i.e. that the exchange interaction of electrons in the pair is independent of time and hence of the distance between the radicals. Secondly, the molecular dynamics of the pair, described by the distribution of diffusion paths of the radicals and the probability of the latter meeting again after their diffusion separation, is described by the Noyes semi-empirical function, which depends on a power of the time $t^{-\frac{3}{2}}$. These assumptions enable spin dynamics (i.e. the dynamics of the singlet–triplet evolution of the pair) and molecular dynamics (i.e. the dynamics of diffusion displacements) to be treated separately, independently. As has been shown above, the result of their combined action, leading to nuclear polarisation, can be presented in comparatively simple analytical form, convenient for the analysis of experimental data, physically clear, and easily interpreted.

However, the hypothesis that spin and molecular dynamics are independent is in general incorrect. The diffusion of the radicals in the pair modulates the mutual orientation of and the distance between the radicals, and consequently modulates the exchange potential. The latter in turn influences the rate of triplet–singlet evolution. Through the exchange potential the molecular dynamics thus has a strong influence on the spin dynamics and hence on the polarisation produced.

A rigorous, non-empirical theory should consider spin and molecular dynamics together, i.e. should solve the problem of the singlet–triplet evolution of a pair with a time-dependent spin Hamiltonian, which in turn controls the molecular dynamics and is a random function of time. Such a non-empirical approach has recently been developed by Freed and Pedersen[19], who have obtained an exact solution of the problem of the $S-T_0$ evolution of a pair and have calculated both nuclear and electron polarisation. It is significant that these authors have used the physically most real model, in which the energy of exchange interaction depends exponentially on the distance between the radicals, while the time dependence of the inter-radical distance is determined by random diffusion and is described by Liouville's stochastic equation. Numerical solution gave polarisation coefficients as functions of various parameters (diffusion coefficients, hyperfine interaction energies, differences in Zeeman energies, parameters of the exchange potential). The problem of the influence of the Coulombic and exchange potential on molecular-diffusion dynamics and on the polarisation has also been solved.

The results of the Freed–Pedersen theory are important in all respects, in particular for the chemical polarisation of nuclei, as the rigorous theory has confirmed the main principles and physical ideas of the semi-empirical theory. Moreover, it has shown that the postulated independence of spin and molecular dynamics does not present a difficulty and does not distort at all seriously the true physical picture of the phenomenon. The physical reason for the insensitivity of the spin dynamics to the exchange potential is that the singlet–triplet evolution is a slow process, so that during its progress the radicals of the pair are able to separate to considerable distances, at which their exchange energy can be neglected. In other words, the main contribution to the singlet–triplet evolution of a pair and to the consequent nuclear polarisation is made by long diffusion paths, on which the exchange potential is negligible. This constitutes an important difference between nuclear and electron polarisation: the former is produced in long-range diffusion paths, whereas short-range spin dynamics makes the major contribution to the establishment of electron polarisation.

The practical (or rather technical) advantage of the semi-empirical theory is that it will give more reliable results, which are simple to interpret physically. The semi-empirical theory contains several parameters (such as the coefficient m in the Noyes function, the probability of recombination in a contact singlet pair ϵ, and the fraction of primary recombination α), of course, but the number of such empirical parameters in the non-empirical theory is no less and even greater. Comparison of the two theories indicates that the semi-empirical theory describes satisfactorily the physics of the phenomenon of chemically induced polarisation of nuclei and gives quite reliable quantitative results. However, this theory requires further development, the empirical parameters must become more accurate, and fresh experiments must be undertaken aimed at further improving and refining the theory.

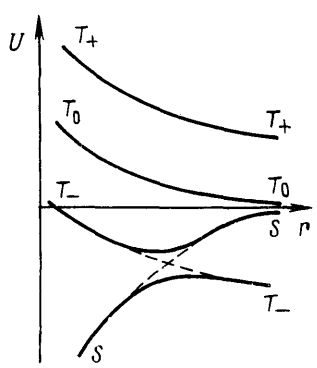


Figure 4. Dependence of energy of spin states of a radical-pair on the inter-radical distance. Full curves show adiabatic reaction paths for recombination (or dissociation) with change in the electron spin; the broken lines represent non-adiabatic paths with conservation of spin.

Besides establishing the physical mechanisms of the non-equilibrium pumping of Zeeman nuclear levels, the chemical polarisation of nuclei has also presented several fundamental results relating to the chemical physics of elementary chemical processes. Firstly, it has confirmed the concepts of the primary and secondary recombination of radicals in a pair and the molecular dynamics of a pair. The quantitative agreement between experiment and theory shows that the function f(t) reproduces quite well the dynamic behaviour of a pair.

Both quantitative agreement with theory and direct experimental results have demonstrated that the intrinsic angular momenta are preserved in elementary radical reactions involving the transfer of atoms (substitutions) and electrons, as well as in the addition of radicals: i.e. such reaction take place with complete conservation of electron and nuclear spins. This is indicated also by the maintenance of spin multiplicity in the transformation of pairs occurring on the decomposition of one of the radicals or on substitution: the resulting new radical-pair retains the spin multiplicity of the old pair. These direct experimental facts, together with the quantitative agreement between theory and experiment, show that the contribution by acts of dissociation and of actual recombination (i.e. "collapse" of the pair) to the establishment of nuclear polarisation is infinitesimal: i.e. these acts occur with conservation of the spins of electrons and nuclei. The behaviour of the energy levels of the dissociating molecule (or, what is the same, the collapsing radical-pair) is shown in Fig. 4. The conservation of the spins of electrons and nuclei as the system moves along the reaction coordinate of dissociation (with increase in the distance r) or recombination (in the opposite direction) shows that the region of quasi-intersection of T_- and S levels (in which $J \simeq g\beta H$) is traversed rapidly, non-adiabatically. For this reason adiabatic effects are insignificant in producing nuclear polarisation[3].

Finally, it must be noted that the spin correlation of electrons, a kind of spin "memory", is preserved in radical-pairs in a liquid for a long time ($\sim 10^{-6}-10^{-7}$ s). The spin correlation is lost in the time interval during which the state of the pair passes into those of the individual radicals. This time is found to be sufficiently long for the radicals to separate to great distances, while retaining the spin "memory" and phase relations of the initial pair[3].

The quantitative agreement between theoretical and experimental results shows that the chief interactions responsible for the singlet–triplet evolution of radical-pairs are hyperfine and Zeeman. These are the "strongest" interactions, responsible for the non-conservation of electron and nuclear spins in radical-pairs; all other interactions (spin–orbit, spin-rotation, etc.) usually play a subordinate role (although, as we shall see later, these interactions are sometimes extremely significant).

4. Chemical Applications of the Chemical Polarisation of Nuclei

The detection of chemical nuclear polarisation has become a new and powerful method for investigating the mechanisms of chemical reactions, a new and sensitive method of detecting radicals and radical processes, on which much has already been written[3,7,20] and which has made the phenomenon widely known and popular in chemistry. However, it must be clearly understood that the observation of nuclear polarisation in a reaction still does not mean that a radical mechanism is fundamentally involved. Several recent experimental results indicate that the phenomenon often arises either entirely in side-reactions or in a process resembling the main process but constituting only a small part of the latter. Thus investigation of the chemical nuclear polarisation in the thermal isomerisation of 2-alkoxyquinoline N-oxides has shown[21] that the proportion accounted for by a radical mechanism is 0.2–0.7.

Chemical nuclear resonance of phosphorus-31 has shown that organic phosphites react with hydroperoxides by two competing mechanisms—radical and non-radical (molecular or ionic)—where the former reaction path, which induces polarisation of phosphorus-31 nuclei, constitutes only a minute fraction ($10^{-2}-10^{-4}$).[22] In the corresponding reactions catalysed by transition-metal ions it has also been established that the radical path is secondary[23]. Application of the same technique to the reactions of ozone with organic phosphites indicates that radical ozonolysis amounts to only about 5%, the main reaction probably involving biradical states in which nuclear polarisation is not produced[24]. Investigation of the chemical polarisation of nuclei in the products of the fairly unusual reaction of tetra-alkylammonium salts with carbon tetrachloride suggests[25] that it has either an ionic or a nucleophilic mechanism and is accompanied by the formation of unstable intermediate compounds, which initiate secondary radical reactions in which the observed polarisation is produced.

Analysis of the chemical polarisation of carbon-13 in the reaction of quinone diazide with cyclohexylamine reveals strong polarisation of the nuclei in an unstable intermediate triazen[26]. It is concluded that this is formed in non-radical stages of the reaction, and that is polarisation results from subsequent reversible decomposition of the triazen by a radical mechanism.

A common feature of the above examples is that the radical mechanism leading to nuclear polarisation either does not predominate or plays an altogether subordinate part. An entirely new aspect of this technique is the separation of radical and non-radical mechanisms, and sometimes even frank discrediting of radical stages and their role in the reactions.

Chemical nuclear polarisation is the only kinetic method which will distinguish competition between radical and non-radical mechanisms, especially if they yield the same products. It becomes possible not only to distinguish these mechanisms but also to estimate their competition. Thus, if a given product is formed by two paths with constants k_1 and k_2 and polarisation coefficients E_1 and E_2, the observed polarisation coefficient is

$$E = (E_1k_1 + E_2k_2)/(k_1 + k_2) = E_1p_1 + E_2p_2 \ , \tag{39}$$

where p_1 and p_2 are the fractions of the two reaction paths. If the second path is non-radical, $E_2 = 1$ and the second term can be neglected. Having calculated E_1 theoretically, we can then easily find p_1 and p_2 (for greater detail see Ref. 3).

An important role in the mechanisms of radical reactions is often played not only by radicals (and hence radical-pairs) but also by biradicals. It is sensible to distinguish between biradicals having dynamic exchange, in which the exchange interaction is usually weak, from radical centres joined by flexible molecular bridges, so that they are able periodically to move together and apart. As a consequence, such biradicals often behave in chemical reactions like radical-pairs. Biradicals with static exchange, on the other hand, usually have a rigid molecular frame, so that the exchange interaction in them is not modulated by molecular movements and remains constant. The Table shows what nuclear polarisation can in principle be expected in strong and weak fields for reactions involving radicals and biradicals.

Character of nuclear polarisation in radical-pairs and biradicals.

Field	Radical-pairs, and biradicals with dynamic exchange	Biradicals with static exchange
Strong	$S-T_0$ (integral and multiplet)	$S-T$ (integral, with $g\beta H \approx J$)
Weak	$S-T_0$ (multiplet) $S-T$ (integral)	

In order that $S-T_-$ transitions should make a significant contribution to nuclear polarisation it is necessary that the S and T_- levels should have approximately the same energy, i.e. that $g\beta H \simeq J$. Hence it follows that their contribution arises in shorter diffusion paths than that by $S-T_0$ transitions. In biradicals with static exchange, where the exchange energy J is fixed, the polarisation has a "resonance" character and appears in a magnetic field corresponding to the condition $g\beta H \simeq J$. It is thus possible by means of chemical nuclear polarisation to measure the energy of exchange interaction in biradicals having different structures. Interesting examples of this type have been given in Closs[6].

In conclusion let us consider in what reactions chemical nuclear polarisation can be observed and whether any predictions can be made. No definite answer can be given, but several considerations may be adduced. First of all, it is necessary that radicals should be generated in the reaction, either in the main or in a secondary reaction path. "Chemical" intuition is necessary to predict this, but experience shows that this is not infallible: the phenomenon is often observed unexpectedly, where radical mechanisms have not been suggested.

Further, high rates of chemical pumping, comparable with the rates of nuclear relaxation, are necessary for the certain observation of chemical nuclear polarisation. It is good if the reaction takes 3-5 min, and still better if it occurs within seconds. However, this condition is desirable but not necessary: even in slow reactions such polarisation can be observed provided that the polarisation coefficients are sufficiently large. In the decomposition of acyl peroxides, for example, intense polarisation has been observed for an hour and more without additional supply of reactant. A quite strict condition can be formulated: in order that a maximum should be observed on the kinetic curves of chemical nuclear polarisation (and this is the clearest and most unambiguous criterion of detection), the condition

$$|E|k - \beta > 0 \quad \text{or} \quad |E|kT_{1n} > 1$$

must be satisfied. Furthermore, these three fundamental parameters—the polarisation coefficient, the reaction rate constant, and the nuclear relaxation time in the molecule—determine the detectability of the polarisation, while the above relation among them is a criterion of its experimental observation.

IV. ISOTOPE EFFECTS IN RECOMBINATION

As shown in Section III, the probability of triplet-singlet conversion in a radical-pair depends on the energy of hyperfine electron-nuclear interaction. For this reason isotope effects should be observed in the recombination of radicals in pairs. Their magnitude can easily be calculated by means of Eqns. (14) and (23).

We shall consider as illustration the simple example of the recombination of hydrogen and deuterium atoms with the trichloromethyl radical. We suppose for simplicity that the initial states for recombination are triplet pairs and assume that the lifetime of the radicals $\tau \gg \mathcal{H}_{ab}^{-1}$. The probability of recombination can then be calculated from Eqn. (25). We compute the ratio of probabilities as

$$\frac{P_{\mathrm{CHCl_3}}}{P_{\mathrm{CDCl_3}}} = \frac{\sum\limits_{ab} \pi^{1/2}\varepsilon m\,|\mathcal{H}_{ab}^{\mathrm{H}}|^{1/2}}{\sum\limits_{ab} \pi^{1/2}\varepsilon m\,|\mathcal{H}_{ab}^{\mathrm{D}}|^{1/2}} \ . \tag{40}$$

The summation covers all states having $m_{\mathrm{H}} = \pm\frac{1}{2}$ for hydrogen and $m_{\mathrm{D}} = 0, \pm 1$ for deuterium, while

$$\mathcal{H}_{ab} = \langle S|\mathcal{H}|T_0\rangle$$

is defined by Eqn. (7). In weak magnetic fields, when $\Delta g\beta H \ll a$, we find from Eqn. (40) with $a_H = 506$ and $a_D = 77$ oersteds that

$$P_{CHCl_3}/P_{CDCl_3} \simeq 1.75\ .$$

In general, when $\Delta g\beta H$ is comparable with the hyperfine interaction, the effect should depend on the strength of the magnetic field.

Isotope effects in the recombination of any radicals from any pair of precursors can readily be calculated in a similar manner. The largest effects must be expected in recombination from triplet pairs, and the smallest from singlet pairs. It would be interesting to compare predicted and experimental effects if any exist.

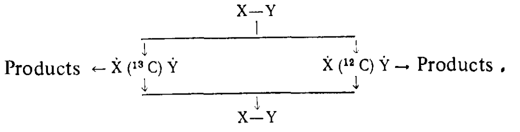
V. ENRICHMENT OF MAGNETIC ISOTOPES IN CHEMICAL REACTIONS

As has been shown earlier—Eqns. (3)-(5) and (7)-(9)—the probability of triplet-singlet transitions in a radical-pair, and hence the probability of recombination, depend on the energy of hyperfine interaction. It depends also on the magnetic moment of the nucleus, since this energy is unambiguously linked with the magnetic moment of the nucleus by the well known Fermi relation

$$a = \frac{8\pi}{3}\mu_e\mu_n\,|\,\psi(0)\,|^2,$$

where μ_e and μ_n are the magnetic moments of the electron and the nucleus, while $|\psi(0)|^2$ is the density of electrons on the nucleus. Thus the probability of a chemical reaction should depend on the magnetic moment of the nucleus, so that chemical reactions can be used for the selection and enrichment of magnetic isotopes, as well as their isolation from non-magnetic isotopes.

This idea can easily be illustrated by a simple example in which triplet pairs are generated chemically (by thermal or photochemical dissociation) from a molecule X-Y:



We suppose that one of the radicals (e.g. X·) contains a carbon nucleus. Radical-pairs containing the magnetic carbon-13 isotope will undergo more rapid triplet-singlet conversion than will pairs containing the non-magnetic carbon-12 isotope. Therefore the former pairs will become singlets more rapidly and recombine more rapidly with the formation of the original X-Y molecules, whereas the triplet-singlet conversion of the latter pairs will lag and such "non-magnetic" pairs will have less chance of recombining. Thus molecules of the initial substance X-Y will be enriched with the magnetic isotope, while the conversion products will be depleted of this isotope.

It is easy to suppose that, if singlet pairs are generated from X-Y, the reverse singlet-triplet evolution of the pairs will result in depletion of the magnetic isotope from the initial molecules, and enrichment of the decomposition products. However, this process will be far less efficient in selecting isotopes, since the majority of the singlet pairs recombine without singlet-triplet conversion (primary recombination), and only a small proportion of singlet pairs undergo singlet-triplet evolution leading to selection of the isotopes. The recombination of triplet pairs is always preceded by triplet-singlet conversion, so that such pairs are most effective in selection. Uncorrelated pairs, formed by the chance encounters of independently generated radicals, occupy an intermediate position with respect to efficiency of isotope selection.

Considering now the quantitative theory of isotope enrichment for the same model pair from X-Y, we suppose that the pair (X·, Y·) is initially in a triplet state and that transitions from the T_- state make the major contribution to its triplet-singlet conversion. The content of the magnetic carbon-13 isotope in the molecule formed from the pair will then be

$$\delta_{S-T_-} = \frac{P^{^{13}C}_{S-T_-}\delta_{^{13}C}}{P^{^{13}C}_{S-T_-}\delta_{^{13}C} + P^{^{12}C}_{S-T_-}\delta_{^{12}C}}\ , \tag{41}$$

where $P^{^{13}C}_{S-T_-}$ and $P^{^{12}C}_{S-T_-}$ are the probabilities of $S-T_-$ transitions in pairs containing carbon-13 and carbon-12 respectively, while $\delta_{^{13}C}$ and $\delta_{^{12}C}$ are the contents of these isotopes in the initial molecules that have not yet undergone chemical change. The numerator of (41) is the probability of formation of X-Y molecules from pairs containing carbon-13; the denominator defines the total probability of the generation of X-Y molecules both from "magnetic" and from "non-magnetic" pairs; and their ratio is the isotopic content of carbon-13 in X-Y molecules formed after recombination. The probabilities of $S-T_-$ transitions are proportional to the squares of the matrix elements of these transitions (Eqns. 5 and 9). On substituting them in (41), we obtain

$$\delta_{S-T_-} = \frac{\delta_{^{13}C}\left[\sum\limits_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C}}{\delta_{^{13}C}\left[\sum\limits_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C} + \delta_{^{12}C}\left[\sum\limits_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{12}C}}\ , \tag{42}$$

where

$$\left[\sum_i \langle T_-|\mathcal{H}|S\rangle_i^2\right]_{^{13}C}$$

is the sum of the squares of the matrix elements over all nuclear spin states of the "magnetic" radical-pair; the second term in the denominator is the corresponding sum for the "non-magnetic" pair.

Considering a numerical example, we suppose a triplet pair (~·C=O, ·CH$_2$~), in which $a_{^{13}C} = 150$ (acyl radical) and $a^H_{CH_2} = 16$ oersteds, with initially the natural isotope content $\delta_{^{13}C} = 0.01$ and $\delta_{^{12}C} = 0.99$. Computing with these values the matrix elements by means of Eqn. (5) or (9) and substituting them in (42), we obtain

$$\delta_{S-T_-} = \frac{[(150/8^{1/2})^2 + 2\,(16/8^{1/2})^2]\cdot 1\cdot 10^{-2}}{[(150/8^{1/2})^2 + 2\,(16/8^{1/2})^2]\cdot 1\cdot 10^{-2} + [2\,(16/8^{1/2})^2]\cdot 0.99} \simeq 0.32$$

i.e. the carbon-13 content in the carbonyl group in the ~CO.CH$_2$~ molecules formed after recombination should have increased more than thirtyfold.

We shall now estimate the contribution of $S-T_0$ transitions to the enrichment of magnetic isotopes. In this case the content of carbon-13 in a molecule generated from a triplet pair by $S-T_0$ transitions is

$$\delta_{S-T_0} = \frac{P^{^{13}C}_{S-T_0}\delta_{^{13}C}}{P^{^{13}C}_{S-T_0}\delta_{^{13}C} + P^{^{12}C}_{S-T_0}\delta_{^{12}C}}\ . \tag{43}$$

Again replacing the probabilities of these transitions by the corresponding matrix elements, we obtain

$$\delta_{S-T_0} = \frac{\left[\sum\limits_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{13}C}\delta_{^{13}C}}{\left[\sum\limits_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{13}C}\delta_{^{13}C} + \left[\sum\limits_i \langle T_0|\mathcal{H}|S\rangle_i^2\right]^{^{12}C}\delta_{^{12}C}}\ . \tag{44}$$

Each of the items in this formula has the same meaning as in Eqn. (42); the sole difference is that the matrix elements are calculated for $S-T_0$ transitions by means of Eqn. (3) for a one-proton pair, or in general by means of Eqn. (7).

However, as we have seen earlier (in analysing the chemical polarisation of nuclei), the probability of an $S-T_0$ transition is proportional to the square of the matrix element only for short-lived radicals: for long-lived radicals the probability is proportional to the square root of the matrix element. This means that Eqn. (44) applies only to short-lived radicals. For long-lived radicals we find from (43) that

$$\delta_{S-T_0}=\frac{\delta_{^{13}\mathrm{C}}\left[\sum_i \langle T_0|\mathscr{H}|S\rangle_i^{1/2}\right]^{^{13}\mathrm{C}}}{\left[\sum_i \langle T_0|\mathscr{H}|S\rangle_i^{1/2}\right]^{^{13}\mathrm{C}}\delta_{^{13}\mathrm{C}}+\left[\sum_i \langle T_0|\mathscr{H}|S\rangle_i^{1/2}\right]^{^{12}\mathrm{C}}\delta_{^{12}\mathrm{C}}}\,. \qquad (45)$$

This equation defines the content of the carbon-13 isotope in a molecule generated by an $S-T_0$ transition from a triplet pair of long-lived radicals.

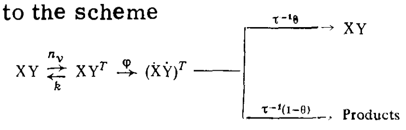
Let us again estimate the contribution made by $S-T_0$ transitions to isotopic enrichment for the same pair ($\sim\!\cdot\mathrm{C{=}O}$, $\cdot\mathrm{CH_2}\!\sim$). Substituting the parameters of this pair in Eqn. (7) and confining our attention to weak fields (i.e. neglecting the term $\Delta g\beta H$), we obtain $\delta_{S-T_0}\simeq 0.29$ for short-lived radicals and the value 0.04 if the lifetime of the radicals in the pair $\tau \gg \mathscr{H}_{ab}^{-1}$.

Enrichment should be most efficient in weak fields, where the contribution to triplet–singlet conversion arises from all three triplet substates; in strong fields only the contribution from T_0-S transitions remains. However, this conclusion must not be regarded as generally applicable: situations may occur in which $\Delta g\beta H$ is large, and then in a strong field $S-T_0$ transitions can play an even greater role in the selection of isotopes than do all three transitions taken together in a weak field.

It is easy also to deduce rigorous equations of isotopic enrichment for cases of recombination in uncorrelated pairs as well as in singlet pairs. It must be borne in mind merely that in singlet pairs primary recombination takes place without isotopic enrichment, so that the isotope content must be averaged over molecules formed by primary and by secondary recombination. Clearly, the greater the probability of primary recombination the smaller the mean isotopic enrichment. For this reason, as has already been noted, the efficiency of selection of isotopes is low in singlet pairs compared with triplet pairs of the same structure.

The above numerical estimates of isotope enrichment apply to cases in which each initial X–Y molecule has undergone only one chemical change, only one act of decomposition. We shall term this the first stage of enrichment. Molecules that have passed through the first stage and are enriched with the magnetic isotope can obviously undergo fresh chemical change and become still more enriched in a second stage; and so on. In fact, with increase in the degree of chemical conversion the quantity of substance X–Y remaining will diminish, but its isotope content will continually increase in proportion to the extent of conversion.

To calculate this effect we suppose that X–Y decomposes at a constant rate (e.g. on photochemical initiation) according to the scheme



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The excited triplet state of the molecule XY breaks down at a constant rate φ to form the triplet pair $(\mathrm{X}\cdot,\ \mathrm{Y}\cdot)^T$, which either recombines again to XY or breaks down and is converted into products; n_ν is the number of quanta absorbed, k the rate constant for deactivation of the triplet state, and $\tau^{-1}\theta$ the constant representing "collapse" of the pair to the original molecule; and θ denotes that fraction of the rate constant that depends on magnetic interactions in the pair. The scheme for conversion of the same molecule XY* containing a magnetic isotope is of the same form, except that the corresponding "collapse" constant is $\tau^{-1}\theta^*$. From the above equations it is easy to express their ratio in terms of the matrix elements of singlet–triplet mixing. If $T_{-}-S$ transition make the major contribution to enrichment, for example, we have

$$\theta^*/\theta=\left[\sum_i \langle T_-|\mathscr{H}|S\rangle_i^2\right]^{^{13}\mathrm{C}}\Big/\left[\sum_i \langle T_-|\mathscr{H}|S\rangle_i^2\right]^{^{12}\mathrm{C}}.$$

Analysis of the kinetic scheme for the concentration variation of "magnetic" molecules XY* and "non-magnetic" molecules XY yields the equations

$$[\mathrm{XY}^*]=[\mathrm{XY}^*]_0-\frac{n_\nu\delta_{^{13}\mathrm{C}}\varphi}{k+\varphi}(1-\theta^*)\,t, \qquad (46)$$

$$[\mathrm{XY}]=[\mathrm{XY}]_0-\frac{n_\nu\delta_{^{12}\mathrm{C}}\varphi}{k+\varphi}(1-\theta)\,t\,. \qquad (47)$$

Since $\theta^*>\theta$, it follows by formal kinetics that a mixture of XY and XY* molecules is enriched with the "magnetic" molecules XY*. The degree of enrichment can be defined as the ratio

$$\delta=\frac{[\mathrm{XY}^*]}{[\mathrm{XY}]+[\mathrm{XY}^*]}\,.$$

Substitution from (46) and (47) yields

$$\delta(t)=\frac{\delta_{^{13}\mathrm{C}}[\mathrm{XY}]_0-\dfrac{n_\nu\delta_{^{13}\mathrm{C}}\varphi}{k+\varphi}(1-\theta^*)\,t}{[\mathrm{XY}]_0(1+\delta_{^{13}\mathrm{C}})-\dfrac{n_\nu\delta_{^{13}\mathrm{C}}\varphi}{k+\varphi}(1-\theta^*)\,t-\dfrac{n_\nu\delta_{^{12}\mathrm{C}}\varphi}{k+\varphi}(1-\theta)\,t}\,. \qquad (48)$$

The extent of conversion χ is defined as

$$\chi(t)=1-\frac{[\mathrm{XY}]+[\mathrm{XY}^*]}{[\mathrm{XY}]_0+[\mathrm{XY}^*]_0}\,.$$

The degree of enrichment will then be related to the extent of conversion by the formula

$$\delta(t)=\frac{\delta_{^{13}\mathrm{C}}[\mathrm{XY}]_0-\dfrac{n_\nu\delta_{^{13}\mathrm{C}}\varphi}{k+\varphi}(1-\theta^*)\,t}{[\mathrm{XY}]_0(1+\delta_{^{13}\mathrm{C}})[1-\chi(t)]}\,. \qquad (49)$$

Clearly, the greater the extent of conversion $\chi(t)$ the higher the isotope content $\delta(t)$, in agreement with qualitative predictions.

Equation (49) holds only when the extent of conversion is not too large, since it takes no account of enrichment in the second, third, etc. stages: i.e. it disregards variation in the initial content of the isotope. For this reason Eqn. (49) gives an incorrect asymptotic approximation as $\chi(t)\to 1$. In principle, however, exact kinetic equations can be deduced for isotope enrichment. The corresponding kinetic parameters n_ν, φ, and k or their combinations can be determined from the kinetics of the consumption of the substance, quantum yields, etc., i.e. from the usual kinetic measurements.

The enrichment of magnetic isotopes in chemical reactions, predicted here and given a theoretical basis, has been detected experimentally[27] in the photolysis of an aliphatic ketone, which becomes enriched with carbon-13. The degree of enrichment increases with the extent of conversion (in conformity with theoretical predictions). This novel principle of isotopic enrichment differs significantly from all other known principles: in none of the latter are magnetic effects in chemical reactions used for enrichment.

The principle of the enrichment of magnetic isotopes in chemical reactions formulated here is quite general and applicable to the sorting of nuclei not only in the carbon-13-12 system but also in other systems (oxygen-17-16, uranium-235-238, boron-10-11, etc.). The efficiency of enrichment is determined mainly by three factors—firstly the convenience of the chemical system (it is extremely desirable that the system should generate triplet radical-pairs), secondly the magnitude of the hyperfine electron-nuclear interaction (it is desirable that the chemical system system should generate radicals having large hyperfine interaction constants), and thirdly the electronic and nuclear relaxation times in the radicals, which should be sufficiently long. If such relaxation is rapid (occurring in times less than or comparable with the duration of triplet-singlet evolution of the pair), spin correlation in the pair is lost rapidly, and the pair remains all the time in an uncorrelated state. In other words, rapid relaxation leads to phase randomisation of the electrons, and prevents the triplet-singlet evolution of the pair from being controlled by hyperfine interaction. As a result, the efficiency of the reaction in selecting magnetic isotopes diminishes. Rapid relaxation in radicals may be caused by strong spin-orbital or spin-rotational interaction (for electrons) and also by quadrupole interaction (for the nuclei).

VI. EFFECT OF A MAGNETIC FIELD ON CHEMICAL REACTIONS

A fourth remarkable consequence of non-conservation of the angular momentum of electrons is that the probability (and the rate) of a chemical reaction depend on the strength of a steady magnetic field. This relation is predicted for radical reactions by Eqns. (3) and (7), according to which a magnetic field changes the probabilities of triplet-singlet transitions in radical-pairs. The effect of a field can be estimated by means of the equations deduced for calculating the chemical polarisation of nuclei.

The probabilities of the generation of molecules from triplet, singlet, and uncorrelated pairs are given by the equations

$$P^T = \sum_{ab} \pi^{1/2}\varepsilon m\,|\mathcal{H}_{ab}|^{1/2} \tag{50}$$

$$P^S = \alpha + (1-\alpha)\int_0^\infty \varepsilon\,\mathrm{f}(t)\,\mathrm{d}t - (1-\alpha)\sum_{ab}\pi^{1/2}\varepsilon m\,|\mathcal{H}_{ab}|^{1/2} \tag{51}$$

$$P^U = \frac{1}{2}\alpha + \frac{1}{2}(1-\alpha)\int_0^\infty \varepsilon\,\mathrm{f}(t)\,\mathrm{d}t + \frac{1}{2}\alpha\sum_{ab}\pi^{1/2}\varepsilon m\,|\mathcal{H}_{ab}|^{1/2}. \tag{52}$$

Equations (50) and (51) have been obtained by generalising (25) and (26). Since we are now interested not in nuclear polarisation but in the aggregate probability of the generation of molecules in all nuclear spin states, the summations in (50) and (51) have been made over all such states. The deduction of (52) will be found in Ref. 3.

A magnetic field obviously accelerates triplet-singlet evolution and increases the probability of recombination in a triplet pair (provided, of course, that $\Delta g \neq 0$). However, the field accelerates equally the reverse, singlet-triplet evolution, so that the probability of recombination in a singlet pair is diminished. Equation (51) shows that this decrease is greater for smaller α, i.e. the smaller the proportion of primary recombination and the greater the proportion of pairs undergoing secondary recombination, in which singlet-triplet conversion takes place. It follows from Eqn. (52) that recombination in uncorrelated pairs is accelerated by a magnetic field.

In estimating the dependence on a magnetic field of the probability of formation of a molecule we can for simplicity neglect hyperfine interaction and assume that

$$\mathcal{H}_{ab} = \frac{1}{2}\Delta g\beta H .$$

Since we have thus postulated that radicals do not contain nuclear spins, the summation in Eqns. (50)-(52) no longer makes sense in this approximation. For a numerical estimate of the effect we consider only uncorrelated pairs, the most general case in chemistry. With $\alpha = \epsilon = 0.8$ and $m = 10^{-6}$ s$^{\frac{1}{2}}$ we find from Eqn. (52) that

$$(P - P_0)/P_0 \simeq 10^{-3}\,|\Delta gH|^{1/2}, \tag{53}$$

where F_0 and P are the probabilities of recombination in the absence and in the presence of a field respectively. Equation (53) defines the relative effect of a magnetic field. Values of $H = 10^4$ and $\Delta g = 10^{-2}$ (the latter is typical of pairs of organic radicals) lead to $(P - F_0)/P_0 = 10^{-2}$, about 1%, which is, of course, small. An appreciable effect of a field can be expected only in the recombination of radicals having markedly different g-factors, i.e. in exceptional cases.

It would appear at first glance that weak magnetic fields should have no effect, for $\Delta g\beta H$ is small. However, in such fields a significant contribution to the triplet-singlet conversion of a pair is made by transitions from T_+ and T_- substates induced by hyperfine interaction with a probability proportional to a^2. With increase in field strength the T_+ and T_- levels diverge, with an accompanying decrease in the contribution to triplet-singlet conversion made by transitions from them. Therefore the effect of a weak magnetic field on reactions is due to elimination of degeneracy from the triplet levels. This mechanism is significant only when the hyperfine interaction and the contribution of T_+ and T_- states to recombination are large.

The influence of a magnetic field exerted by this mechanism was first observed by Sagdeev et al. in the reaction between perfluorobenzyl chloride and n-butyl-lithium[28-30]. This reaction involves $\cdot CF_2C_6F_5$ radicals, in which the energy of hyperfine interaction with fluorine-19 nuclei is large and the contribution by T_+ and T_- states to triplet-singlet conversion of radical pairs is considerable. No effect of the field has been detected in the corresponding reaction of benzyl chloride, since hyperfine interaction with the protons in the $\cdot CH_2C_6H_5$ radical is weak, and therefore the contribution of T_+ and T_- states to recombination small. For the same reason no effect of a magnetic field has been detected on the photosensitised decomposition of benzoyl peroxide[31].

Thus the influence of a magnetic field on the probability of the recombination of radicals can operate by two mechanisms. Firstly, the relative contributions by S-T_0 and S-$T_\pm$ transitions to triplet-singlet conversion of a pair changes on passing from weak (or zero) to strong fields. If the precursor of the recombination product is a singlet radical-pair, the probability of recombination increases as the field becomes stronger. If the precursor is a triplet or an uncorrelated pair, the probability of recombination diminishes with increase in the field. This mechanism operates only when considerable electron–nuclear hyperfine interaction is present in the radicals. Secondly, if Δg is large in the radical-pairs, the probability of recombination increases in proportion to $|\Delta g\beta H|^{\frac{1}{2}}$ for triplet and uncorrelated pairs, but decreases in proportion to $|\Delta g\beta H|^{\frac{1}{2}}$ for singlet pairs. This mechanism is far more important and will be extended to other reactions.

Both these effects can be calculated theoretically in each case, and the dependence of the probability of recombination on the intensity of the magnetic field can be predicted. In the reactions of organic radicals, however, considerable effects can be expected (cf. the above numerical estimates), because values of Δg are usually small in pairs of organic radicals. Considerably greater effects may be expected in reactions involving transition-metal ions and organic molecules or radicals, when Δg may be considerable. Thus in the pair (Fe^{2+}, O_2), which probably precedes the electron-transfer reaction

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^-$$

for example, $\Delta g \simeq 2$, and with $H = 10^4$ oersteds the effect of the magnetic field may reach ~10%.

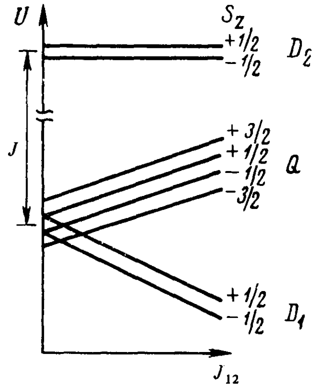

Figure 5. Energy levels and spin states of a triplet–doublet pair (*T*, *D*).

In more complicated reactions involving species in higher spin states (triplets, quartets, etc.) a magnetic field induces transitions between states differing in spin multiplicity. For example, a "triplet + doublet" reaction (an example is the interaction of oxygen in a triplet state with a radical in a doublet state) is preceded by a (*T*, *D*) pair containing three unpaired electrons. Such a pair may exist in states of total spin $\frac{3}{2}$ and $\frac{1}{2}$, corresponding to a quartet and two doublet states (Fig. 5). One of the doublet states (D_2) corresponds to singlet oxygen and is situated at a great height, so that it will be of no interest to us. A magnetic effect arises from the mixing of quartet and doublet states Q and D_1, of substates of Q having $S_z = \pm\frac{1}{2}$ with the corresponding substates of D_1, i.e. of states having the same z-components of the total electron spin. The physical meaning of quartet–doublet mixing is the same as for triplet–singlet mixing in radical-pairs.

A calculation has been made of the effect of a magnetic field in such a system[32]. Since reaction occurs only in the doublet state D_1, it should be accelerated by a magnetic field which induces additional quartet–doublet transitions. Fig. 5 shows that the exchange interaction J_{12} between the electrons of the components of the pair removes the degeneracy of the miscible levels D_1 and Q and slows down the quartet–doublet evolution (just as exchange interaction retarded triplet–singlet evolution in a radical-pair). However, if it is accepted that the molecular dynamics of the pair (*T*, *D*) is the same as for a radical-pair, the exchange interaction J_{12} can be neglected, and the effect of the field is then proportional to $|\Delta g\beta H|^{\frac{1}{2}}$.

The influence of a magnetic field on other, more complicated reactions has been discussed in Ref. 3, where numerical estimates are given of the effects to be expected.

The influence of a magnetic field on biological systems and processes, reported in many papers on magnetobiology, may be due to molecular mechanisms of the above type. Such mechanisms should operate in biochemical reactions involving species having unpaired electrons (e.g. processes involving the transfer of electrons along the chain of cytochromes and the associated reactions of oxidative phosphorylation, many enzymic reactions, the oxidation of non-haemin iron by oxygen, certain stages of photosynthesis, etc.). Experimental results summarised in several monographs of magnetobiology[33-36] show that the effect of a field is most significant in these particular biochemical systems (or in those organelles, e.g. in mitochondria, where these processes take place).

Thus there are clear and soundly based physical reasons for the influence of a magnetic field on the rates of chemical reactions. They are due to the influence of the field on the probabilities of intersystem transitions between states of different spin multiplicities in the reactant-pairs. Even within the framework of this general mechanism, however, the effects of a magnetic field may be extremely diverse, for several reasons.

Firstly, a magnetic field should have no effect if $\Delta g = 0$ in the reactant-pair.

Secondly, the magnitude of the effect is strongly dependent on the molecular dynamics of the reacting pair. Thus in a radical-pair in a liquid the dynamics is described by the function $f(t) = mt^{-\frac{3}{2}}$, so that the field effect is proportional to $|\Delta g\beta H|^{\frac{1}{2}}$. If the dynamics of the pair is described by an exponential function, the effect is proportional to $(\Delta g\beta H)^2$.[3] With reaction between charged species diffusion in the pair takes place in a Coulombic field, and the function $f(t)$ has a completely different form[3]. Magnetic effects may be expected in principle even if the reactant centres are fixed in certain structural units (e.g. in mitochrondrial membranes), and reaction between them (electron transfer) occurs by a tunnel mechanism. Such a mechanism is often assumed in biochemical systems.

Thirdly, exchange interaction between electrons in the reactants forming a pair has a significant influence on transitions between spin states in the pair: the greater this interaction the smaller the effects to be expected. Different situations may arise, of course, in different (especially biochemical) systems: in some cases exchange interaction may be negligible, and in others considerable (as e.g. in the reaction of oxygen with deoxyhaemoglobin to form diamagnetic oxyhaemoglobin). For this reason threshold phenomena are possible, or even a change in sign of the effect with change in intensity of the magnetic field.

Fourthly, the observation of magnetic field effects requires that intersystem transitions between states of different spin multiplicities in the reacting pairs should be induced by a difference in Zeeman energies $\Delta g\beta H$, and this requires that the electronic relaxation times of the components of the pair should be sufficiently long: otherwise, rapid electronic relaxation will lead to randomisation of the precession phases of the electrons and disrupt evolution of the pair from one spin state to another. Such loss of spin correlation in a pair because of rapid electronic relaxation would lead to a loss of magnetic effects. (As shown in Section V, the efficiency of selection of magnetic isotopes in chemical reactions decreases markedly for the same reason.)

The problem of the effect of a magnetic field on chemical and biochemical processes has a long and rich history; much and often contradictory information has been obtained on magnetobiology and magnetomedicine. Examination shows that much of it is naive and physically unsound, and often it is erroneous. However, there is also a considerable proportion of reliable results, showing convincingly that magnetic effects in chemical and biological processes are real and frequently significant. It would be interesting to consider such data from the viewpoint of the molecular mechanisms discussed here, test several predictions following from these mechanisms, and also set up experiments at a molecular level.

VII. CONCLUSION

The intrinsic angular momentum of both electrons and nuclei is conserved in elementary chemical reactions involving substitution, dissociation, recombination, electron transfer, addition, disproportionation, etc: i.e. these elementary processes take place without change in the spins of electrons and nuclei. This conclusion applies equally to homolytic and to heterolytic reactions, as is directly indicated by results for the chemically induced magnetic polarisation of electrons and nuclei.

The reason for the conservation of spin in elementary chemical processes is that their duration is extremely short, around 10^{-14}–10^{-13} s. This is considerably less than the reciprocal of the rates for all the interactions that are able to induce change in the spin of an electron or a nucleus during a chemical process.

If in a chemical reaction, however, long-lived states are established, in which transitions are possible between levels differing in spin multiplicity, the intrinsic angular momentum of electrons and nuclei is not conserved in such states. A clear example is provided by the radical-pairs that precede chemical acts of recombination or disproportionation. Their lifetime (10^{-11}–10^{-8} s) is sufficiently long for transitions between states differing in spin multiplicity (triplet and singlet), accompanied by changes in electron and nuclear spins. This time is already comparable with the reciprocal of the interaction that induces transitions between singlet and triplet. (Quite weak interaction, e.g. an external radio-frequency field H_1, is able to change the angular momentum of electrons and nuclei. The energy of interaction of the field with an electron or a nucleus is γH_1, where γ is the gyromagnetic ratio for the electron or the nucleus. However, a longer time, of the order of $(\gamma H_1)^{-1}$, is now required to change the spin. Thus with $H_1 = 1$ oersted the time necessary for reorientation of an electron or a proton is respectively $\sim 4 \times 10^{-7}$ and 3×10^{-4} s. Such a change in spins is the essence of the phenomena of electron spin resonance and nuclear magnetic resonance.)

A long period of existence of radical-pairs (or reactant-pairs in general, with a set of electron-spin states) is not the sole condition ensuring the non-conservation of spin. Another important condition is that the exchange interaction between the electrons of the components of the pair should be sufficiently weak. Strong exchange interaction stabilises the angular momentum, maintains the electron spin of the system, and suppresses the evolution of the pair from one spin state to another.

Finally, a third condition is an interaction that induces transitions between spin states and alters the angular momentum. As shown above, the most important of this type are Zeeman and hyperfine interactions. The latter is especially important in weak fields, where the bonding between electron and nucleus is stronger than that of electrons and nuclei with the external magnetic field. Electron and nucleus then behave as a single spin system, change in the electron spin being balanced by a simultaneous change in the nuclear spin.

If all three conditions are satisfied, the angular momentum of the electrons and nuclei in a chemical system may not be conserved. This leads to magnetic effects in chemical reactions, the most striking of which are the chemical polarisation of nuclei, the enrichment of magnetic isotopes in chemical reactions, and the effect of a magnetic field on the rates of chemical reactions.

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Reactions in Frozen Multicomponent Systems

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Results of research on chemical reactions in frozen multicomponent systems are summarised. Transition of a system into a peculiar solid state leads to the appearance of several characteristic features, which can be explained on the basis of a structural-kinetic model. A list of 104 references is included.

CONTENTS

I. INTRODUCTION

Investigations on the kinetics and the mechanism of chemical reactions in ordered systems, in particular at low temperatures, constitute a new and rapidly developing branch of chemistry. The attention and interest of world science was directed to this field mainly by Soviet scientists, primarily Academician N. N. Semenov. In his contributions to the International Symposium on Macromolecular Chemistry at Moscow in 1960[1] and to the Eighteenth International Congress of Pure and Applied Chemistry at Montreal in 1961[2] he summarised experimental results, obtained by that time by several Soviet scientists, on low-temperature polymerisation, formation and destruction of free radicals, and rapid chain reactions in the photochemical hydrobromination of alkenes.

Semenov had studied chemical reactions in the solid phase at low temperatures as early as the 1920s. When sulphur and cadmium vapours produced deposits on a surface cooled in liquid air, explosive formation of cadmium sulphides was observed when the layer reached a certain thickness[3,4]. The method of molecular beams, proposed in these papers for the study of reactions at low temperatures, has since been successfully applied to the investigation of polymerisation[5-7] and the halogenation of alkenes[8].

At the end of the 1950s Semenov, with his ever present sense of the novel, gave active support to investigations, begun in the Department of Chemical Kinetics directed by him at Moscow State University, on the chemical reactions of halogens and hydrogen halides with various substances at temperatures close to the boiling point of nitrogen. This work revealed that in some cases lowering the temperature may favour a chemical process, and a reaction that does not take place at room temperature may be accomplished at low temperatures. It was discovered that certain chemical processes occurred spontaneously and rapidly at low temperatures, that chain reactions could take place in the solid phase, and that phase transitions and unstable molecular complexes of donor-acceptor type played a special role in effecting chemical changes at low temperatures. The results have been summarised in reviews[9-12]. These investigations, combined with studies of initiated and non-initiated polymerisation at low temperatures, and the formation and conversion of free atoms and radicals, established the foundations of a new branch of chemical physics—cryochemistry.

The accomplishment of chemical changes in the solid phase at low temperatures considerably extends our views on the elementary act in a chemical process. Transition of a reacting system from the gaseous to the liquid and solid states is accompanied by the intensification of intermolecular interactions, which begin to play an important part. Unstable reactive species can be investigated at low temperatures. Cryochemistry opens the way to obtaining and studying unstable intermediates involving radicals, ions, and reactive molecules, a path to the synthesis of new chemical compounds that are difficult or quite impossible to obtain in other ways.

The reaction having the lowest activation energy is most likely to occur at low temperatures. Hence a kind of energy selection may occur, leading to the formation of only one chemical product in a series of parallel processes. This will permit the establishment of a new chemical technology, characterised by the controlled synthesis of required products. At low temperatures substances can be obtained in a high degree of purity, uncontaminated by side-products and without poisoning the environment.

Until not long ago attention was paid mainly to photochemical and radiation-chemical processes in the study of chemical reactions at low temperatures. These aspects were analysed by Semenov[1,2] and in several other monographs and reviews[13-15].

Two periods—from the end of the nineteenth century to the middle of the 1950s and from the end of the 1950s to the present time—can be traced quite clearly in the investigation of chemical reactions at low temperatures. Mainly haphazard and qualitative work was undertaken during the first period; it has been surveyed in monographs[16,17]. Systematic investigation of different chemical reactions at low temperatures began during the 1950s, after it had been established that active atoms and radicals are stabilised at the temperature of liquid helium[16,17].

At the end of the 1950s research on low-temperature polymerisation was begun both here and abroad[1]. At the same time studies were begun in Moscow University on the addition of halogens to double bonds at temperatures close to 77 K.[18] It was discovered in the early 1960s that chemical and biochemical processes can occur in frozen solutions at temperatures below the melting point of the solvent[19]. The conversion of various monomers at low temperatures, the generation and transformation of radicals in solids, and low-temperature reactions of halogens and halogen hydrides with alkenes and cyclic compounds are being investigated in many Soviet institutes and laboratories. A systematic study of such processes has been made in Moscow University.

Research during recent years has shown increasingly clearly that detailed knowledge of the phase condition of ordered systems is necessary for an understanding of the mechanism of chemical changes occurring in them. It is extremely important to examine the formation and the development of defects in solids and to establish the relation between these processes and change in the reactivity of the system. The effect of the heterogeneity of a specimen on the occurrence of chemical reactions in it should be most clearly evident in multicomponent systems.

Research at Moscow University during recent years has shown that many kinetic rules governing chemical processes occurring in frozen multicomponent systems can be understood if the liquid phase is considered to constitute the defects responsible for the chemical reactions. Conditions for the formation of such a phase may be produced in multicomponent systems during preparation of the specimens or at the instant of reaction.

The study of solid multicomponent systems, in particular frozen solutions, is of great practical interest. This is connected primarily with problems in the low-temperature preservation of food products and of biological and medical preparations.

The present Review surveys several chemical and biochemical reactions occurring in multicomponent systems, especially in frozen solutions. These belong to an important class of solid-phase processes possessing several specific features.

II. TYPES OF REACTIONS AND PROCESSES

Investigators working at low temperatures are faced with several difficulties. Analysis of the reaction products must usually be carried out after the system has warmed up to room temperature. This involves a phase transition, during which the mobility of the molecules increases and various processes can easily occur[1,2], which must be taken into account. Douzou et al. have shown[20,21] that fall in temperature is accompanied by abrupt changes in such macroscopic properties of the system as its dielectric constant, viscosity, and hydrogen-ion concentration.

The first investigations of reactions involving at least two substances were usually made in vacuum equipment with layer-by-layer freezing of the reactants. The progress of the reaction was followed thermographically, and various chemical and physicochemical methods of analysis were applied after warming to room temperatures[10,22]. However, reactions under such conditions yield insufficiently homogeneous mixtures, so that it is difficult to obtain quantitative results.

The method of molecular beams[8,23] enables homogeneous multicomponent mixtures to be obtained at low temperatures. Combining it with spectral or calorimetric measurements gives information on the composition of the products and on the effective activation energy[11,24]. Condensation in molecular beams and the method of matrix isolation are used also to investigate photochemical processes[25]. Special designs of cuvettes and cryostats together with spectral methods of analysis enable the composition of the products to be studied, and in several cases also the kinetics of their formation, directly at low temperatures[26]. Inert vitrifying solvents can conveniently be used here.

Experimental studies of reactions in frozen solutions are usually made[27] by running together solutions of the reactants and freezing rapidly in liquid nitrogen. The specimens are then placed in a cryostat at the experimental temperature, with allowance for the effect of establishment of the temperature in the specimen and occurrence of the reaction during warming up. In a kinetic study chemical or physicochemical analyses of a series of specimens are made at definite time intervals. Electron spin resonance can be employed for processes involving stable radicals, to give data on reaction kinetics directly at the experimental temperature, without heating of the specimen[28]. Fig. 1 shows as example the temperature dependence, obtained by the above technique, of the rate of reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl with hydrazobenzene.

Table 1 gives experimental results for various chemical and biochemical reactions occurring in multicomponent systems at low temperatures. Polymerisation, photochemical and radiation-chemical reactions, and processes involving stabilised radicals are not included, since they fall outside the scope of the present Review. It is evident that the most diverse types of processes can be accomplished at low temperatures in frozen solutions, with and without solvents.

III. KINETIC FEATURES

Analysis of experimental results obtained for various chemical processes at low temperatures will reveal several of their common and most characteristic features. The temperature dependence of reaction velocity illustrated in Fig. 1 is typical of the frozen multicomponent systems listed in Table 1. Reaction occurs below the freezing point of the solvent, and takes place formally in the solid phase. Several experiments have shown that a process is more rapid in frozen solutions than e.g. in supercooled liquid solutions at the same temperature[28]. Fig. 1 shows the extremal temperature dependence of reaction velocity in frozen solutions. The rate of reaction in a solid matrix at a lower temperature is greater than in the liquid phase. Thus transition of a system from the liquid phase to the frozen state is accompanied by increase in the rate of a process: i.e. the phenomenon of a negative temperature coefficient is observed.

The most characteristic feature of reactions in binary systems, which have been investigated at low temperatures mainly in the absence of a solvent, is the influence of phase transitions. Most of the mixture usually reacts when one of the starting materials melts. If the reactants undergo phase transitions below the melting point of the mixture, reaction may take place in the solid phase. In the cyclohexene–chlorine system, for example, reaction occurs at −170°C, at the instant of transition of cyclohexene from a vitreous to a crystalline state[8,23].

In the absence of solvents, chemical reactions occur readily at low temperatures, at high rates, and usually give a single product in nearly theoretical yield[10]. In order to elucidate the mechanism several reactions between halogens and alkenes have been studied in non-polar solvents over a wide temperature range. The characteristic kinetic feature under such conditions is a negative temperature coefficient[12,29]. Increase in rate with fall in temperature has recently been observed for the reaction of nitrosyl chloride with α-oxides[30] and in those between halogens and phenylcyclopropanes[31].

Table 1. Chemical reactions in frozen solutions and at low temperatures.

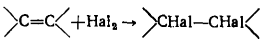
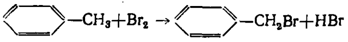
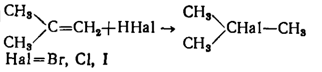
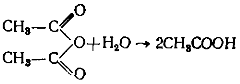
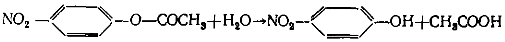
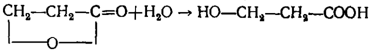
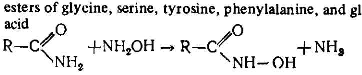
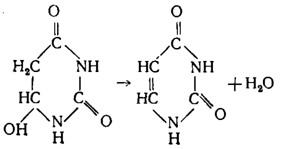
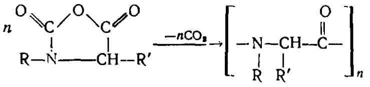
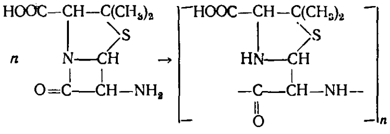
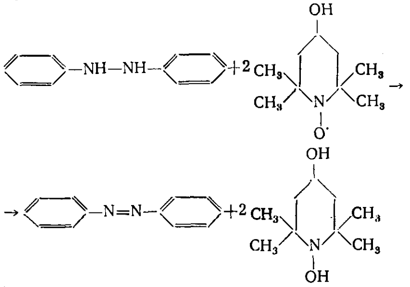
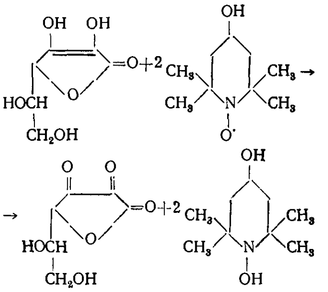
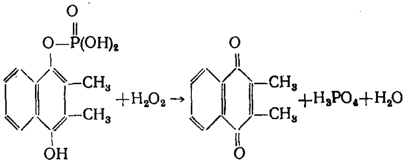
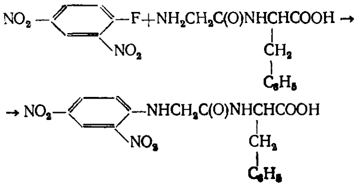
No.	Process	Reaction, substance (catalyst)	Solvent	t, °C	Ref.
1	Halogenation of alkenes and aromatic compounds	 ethylene, propene, isobutene, cyclohexene, hex-1-ene halogens: chlorine, bromine	none	—45——196	9, 18, 84
		bromination of hex-1-ene	cyclohexane, benzene	0——110	42
		bromination of toluene 	none	—70——142	9
2	Reaction of alkenes with NO_2	alkenes: propene, isobutene, but-1-ene, hex-1-ene, cyclohexene, cyclopentadiene, buta-1,3-diene; main products: dinitroalkanes, nitroalkyl nitrites and nitrates	none	0——90	9
3	Inorganic addition and exchange substitution	$2NO+Cl_2 \longrightarrow 2NOCl$ $HBr+Cl_2 \longrightarrow HCl+ClBr$ $2NO+O_2 \longrightarrow 2NO_2$	none	—116——165 —105——182 —95	9
4	Hydrohalogenation of alkenes	 Hal=Br, Cl, I	none	—100——190	9
5	Hydrolysis	acetic anhydride  *p*-nitrophenyl acetate  *β*-propiolactone (catalyst: imidazole) 	water	—10	85
		δ-thiovalerolactone and γ-thiobutyrolactone (morpholine)	water	-10 to 45	85, 86
		penicillins G and V, 6-aminopenicillanic acid (imidazole, histidine, histamine, carnosine, OH^-)	water	to -78	19
6	Hydroxylaminolysis	formamide, acetamide, propionamide, asparagine, glutamine, 2,5-diketopiperazine, cytosine, acetylcholine; esters of glycine, serine, tyrosine, phenylalanine, and glutamic acid 	water	to -23	60, 65, 87, 88
		ethyl ester of lysine, methyl esters of lysine and arginine (trypsin)	water	—18	89
7	Inhibition by structural analogues (in hydroxylaminolysis)	esters of phenylalanine, serine, lysine, tyrosine, and glutamic acid; other cpd.	water	—18	90
8	Decomposition	hydrogen peroxide ($CuCl_2$, $FeCl_3$) $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	water		91
		t-butyl peroxyformate (2,6-lutidine, pyridine) $HC(O)OOC(CH_3)_2 \rightarrow HOC(CH_3)_3+CO_2$	*p*-xylene	to —70	92, 93
9	Menshutkin reaction	$CH_3I+(C_2H_5)_3N \rightarrow [(C_2H_5)_3NCH_3]I$	benzene, nitrobenzene, dioxan, CCl_4, water	to —196	42, 94 44, 61—64
10	Formation of epoxides	2-chloroethanol (reaction with NaOH)	water	to —15	95
11	Mutarotation	glucose (HCl)	water	—7	96
12	Dehydration	5-hydro-6-hydroxyuridine 	water	—10	72
13	Electron transfer	$Fe^{3+} \rightleftarrows Fe^{2+}$	water	to —196	97
14	Polymerisation	anhydrides of *N*-carboxyamino-acids 	dioxan	to —26	98
		6-aminopenicillanic acid 	water	to —28	99
		adenosine cyclic 3′,5′-phosphate,	water	—15	100
		oligo(2′-*O*-methylinosine 3′-phosphate) (on poly-C matrix)	water	—15	101

Table 1 (Cont'd.)

No.	Process	Reaction, substance (catalyst)	Solvent	*t*, °C	Ref.
15	Oxidation	hydrazobenzene 	dioxan	to —196	42, 44
		ascorbic acid 	water	—30 to 40	42
16	Enzymic oxidation	phosphoric esters of quinols (peroxidase) 	water	—30 to 50	65
17	Nucleophilic substitution	fluoro-2,4-dinitrobenzene with glycylphenylalanine (hexadecyltrimethylammonium bromide) 	water	—30 to 30	83
18	Chemical inactivation of enzymes	trypsin with imidazole α-chymotrypsin with urea	water water	—18 to —70	102 103
19	Denaturation of DNA	in solutions buffered at various pH	water	—13 to 25	104

Reactions with halogens are characterised by the formation of unstable intermediate donor–acceptor complexes of diverse composition and structure. The role of such complexes has been discussed in great detail[12], as well as the participation of complexes in the formation of radicals[32]. A negative temperature coefficient can be regarded as kinetic evidence that molecular complexes are involved in the chemical reaction. The participation of unstable donor–acceptor complexes will explain the main features of chemical reactions occurring at low temperatures in the absence of a solvent or in a non-freezing solvent. This concept is also extremely useful for analysing the mechanism of reactions of many different organic compounds[33].

Various hypotheses, usually without adequate experimental support, have been adduced to explain the features of chemical reactions in frozen multicomponent systems. The acceleration of chemical processes in frozen solutions has been attributed to change in the reaction mechanism, catalysis by the surface of the solid phase, the occurrence of phase transitions, the presence of various defects, the concentrating of reactants in non-freezing regions of the solvent, the existence of molecular compounds, a favourable spatial arrangement of the reactants, and an increase in the mobility of protons in ice. In the Reviewers' opinion the decisive role belongs to structural inhomogeneity and the consequent high mobility of the reactant molecules.

IV. STRUCTURAL AND PHASE INHOMOGENEITY

The variety of chemical processes occurring at low temperatures and the similarity of their inherent features indicate that the course of chemical reactions in frozen solutions is influenced by quite general factors. The occurrence of a reaction requires a certain degree of mobility of the molecules; it is impossible to understand the reasons for the acceleration of chemical changes and to elucidate their mechanism without knowledge of the structure and the phase constitution of the frozen solutions. Unfortunately, the structure of frozen solutions has not been adequately studied, and hardly any data are available on the phase state and the molecular mobility in such systems under the reaction conditions.

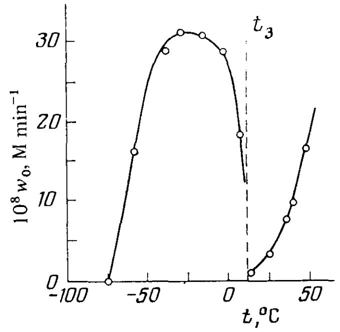


Figure 1. Temperature dependence of rate of reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl (R) with hydrazobenzene (Hab) in liquid and frozen dioxan solutions, with $[R]_0 = [Hab]_0 = 10^{-4}$ M.

Structural heterogeneity of frozen aqueous solutions was detected in the investigation by electron spin resonance of the distribution of paramagnetic ions—VO_2^{2+}, Mn^{2+}, and Gd^{3+}—at the temperature of liquid nitrogen[34-38]. Analogous results were obtained in a study of solid solutions of organic compounds by the method of stable radicals[39,40]. In solid solutions of sulphuric acid of concentration > 3.5 M the distribution of vanadyl ions is almost uniform, whereas in specimens that freeze as polycrystals a non-uniform distribution of these ions is observed.

The phase constitution of about ten binary systems has been studied by e.s.r.[28,41-43] with the stable 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl radical as tracer, varying in concentration from 10^{-7} M to 2×10^{-4} M. Analysis of the structure was based on the difference between the spectra of the radical in solution and in the solid state. Binary and ternary solutions of various compositions were examined over a wide temperature range, from 40 to −196°C. Solutions consisted either of the solvent and the tracer radical or of solvent, additive, and radical. The solvents used were water, dioxan, benzene, nitrobenzene, hexane, cyclohexane, etc. Substances having freezing points both above and below that of each solvent were chosen as additives—other solvents and also iodomethane, triethylamine, hydrazobenzene, azobenzene, hex-1-ene, ascorbic acid, inorganic salts, and other substances.

In all the systems investigated the e.s.r. spectrum of the tracer radical at −18°C is a triplet. The correlation times τ suggest that the mobility of the radical in frozen solutions at this temperature is comparable with its mobility in the liquid phase. As example Fig. 2 shows the spectra in three systems. The combined results indicate that frozen multicomponent systems are heterogeneous with respect to structure and, what is especially important, phase. Such systems are characterised by the coexistence of two phases—solid and liquid—over a very wide temperature range. One of these phases has been termed[44] a liquid microphase, to emphasise the abnormally high molecular mobility in this phase.

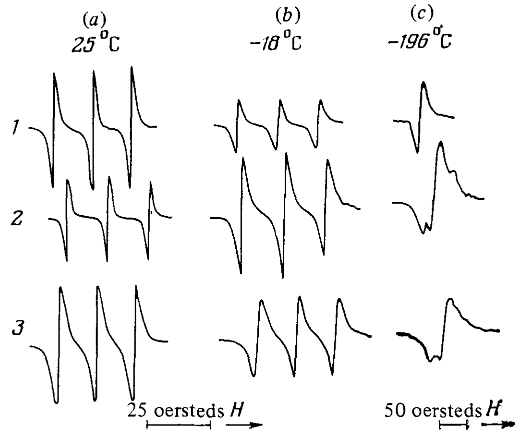


Figure 2. Spectra (e.s.r.) of 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl in: *a*) liquid; *b*), *c*) frozen 10^{-5} M solutions in various solvents: 1) dioxan (m.p. 11.8°C); 2) water (0°C); 3) cyclohexane (6.5°C). Correlation times ($10^{12}\tau$, s): 1*a*) 3.3; 1*b*) 66; 2*a*) 23; 2*b*) 130; 3*a*) 5.0; 3*b*) 16.

The existence of regions of high mobility has since been detected in an investigation of electronic spin–lattice relaxation times T_1 and e.s.r. spectra of frozen aqueous solutions of paramagnetic ions[45]. In aqueous (0.5 M) manganese(II) nitrate solutions high mobility is preserved down to −50°C. In this system the relaxation time T_1 increased sharply when the temperature changed only slightly, from 4.1×10^{-9} to $\sim 3 \times 10^{-8}$ s between −50 and −57°C.[45] Cooling from one temperature to the other was obviously accompanied by freezing of the liquid microphase, when the whole specimen became in fact solid.

The e.s.r. spectrum of diphenylpicrylhydrazyl shows a sharp increase in line width near the setting temperatures of solutions in toluene[46]. This is due to displacement of the hydrazyl radicals into uncrystallised regions and increase in their local concentration. The bell-shaped temperature dependence of the intensity ratio of e.s.r. spectra due to radical-pairs having a transition $\Delta M_S = 2$ and to radicals having the transition $\Delta M_S = 1$ in frozen solutions (10^{-3} M) of the stable 2,2,6,6-tetramethylpiperidino-oxyl radical in cyclohexane is also caused by structural heterogeneity of the system and the formation of liquid microregions on freezing[47].

Recent results have indicated the existence, on the surface of ice below 0°C, of a quasi-liquid layer in which the coefficient of self-diffusion of water molecules is as much as 10% of the value in liquid water under normal conditions[48]. Abnormally high mobility of water molecules is observed in frozen solutions of biopolymers, and is usually attributed to a special state of water in the hydrate sheath[49,50].

Electron spin resonance enables only a paramagnetic component to be followed. More complete information on the composition of the liquid microphase is obtained by nuclear magnetic resonance[42,44], the theory of which indicates[51] that absorption lines in solids are broader than those in the liquid phase and are not recorded in high-resolution n.m.r. spectra. If a liquid microphase is formed in a frozen solution, in which reactants are concentrated, narrow resonance lines must be expected to appear in the high-resolution n.m.r. spectra of such solutions, corresponding to reactants that retain their mobility and to part of the solvent. Comparatively narrow resonance signals due to solutes and solvent are indeed observed in frozen solutions[28,52].

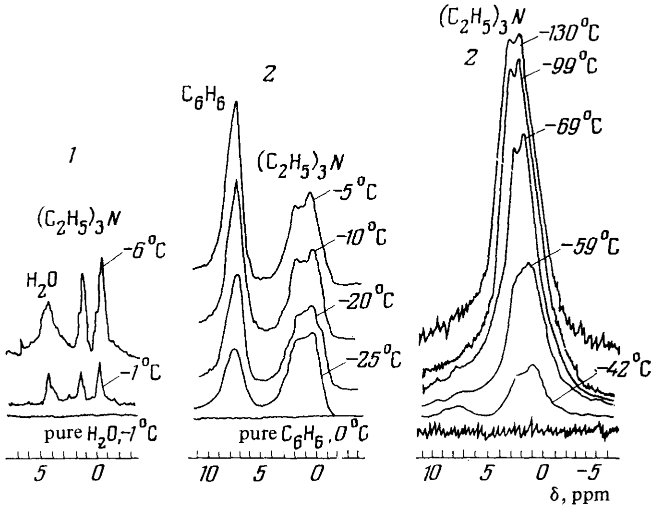


Figure 3. Spectra (n.m.r.) at various temperatures for frozen pure solvents and solutions of triethylamine: 1) 0.04 M; 2) 0.4 M.

Fig. 3 shows as example high-resolution n.m.r. spectra for frozen solutions of triethylamine in water and in benzene. It is evident that the pure solvents do not give such spectra when frozen. The spectra of the frozen solutions contain absorption bands corresponding to triethylamine and to the solvent. A frozen solution is found to contain highly mobile triethylamine molecules down to −130°C.

Integration of the n.m.r. spectra has enabled the temperature variation of the composition of the liquid microphase to be traced. The temperature dependence obtained for the ratio of the numbers of moles of iodomethane and benzene $P_{CH_3I}/P_{C_6H_6}$ in the liquid microphase of frozen benzene solutions and in the liquid solution (0.4 M CH_3I) is given in Table 2. The absolute numbers of moles of various substances in the liquid microphase have been calculated by comparing the results of integrating their spectra and those of a standard, a sealed capillary containing a concentrated solution of sulphuric acid. It is found (see also Fig. 3) that a liquid microphase, consisting of part of the solvent and solutes, is present in frozen solutions down to several tens of degrees below the melting point. Fall in temperature is accompanied by decrease in volume of the liquid microphase, as solvent freezes out and the concentration of the solutes increases.

Table 2.

t, °C	25	−29	−47	−59	−80
	liquid solution		frozen solutions		
$P_{CH_3I}/P_{C_6H_6}$	0.036	1.6	3.3	4.4	15.4

The composition of the microphase depends on the temperature, the proportion of solute increasing with fall in temperature. Table 2 shows that the ratio of the quantity of iodomethane to that of benzene in the liquid microphase of frozen solutions changes by factors of 8.5 and 370, relative to the liquid solution at 25°C, when the temperature falls to −29 and −80°C respectively. In this case we may consider that benzene is dissolved in iodomethane in the liquid microphase, since this contains far more of the latter than of the former.

The composition of the liquid microphase at a given temperature remains unchanged when a specimen is cooled from room temperature to −130°C and then allowed to warm up until the solution has completely thawed out. When the specimen is cooled to −196°C, the liquid microphase gradually disappears: i.e. molecules in the microheterogeneities lose their high mobility. The liquid microphase reappears when the specimen warms up. Comparison of specimens that have first been frozen in liquid nitrogen with those that have not been immersed in it but have been frozen in the resonator of the spectrometer at the specified temperature has shown that formation of the liquid microphase is independent of the method of freezing: it has the same composition in the two cases.

The temperature range of existence of the liquid microphase, the degree to which solutes are concentrated in it, and its volume at a given temperature are determined by the quantity of solutes and by the physicochemical properties of the system, of which the most important are the cryoscopic properties of the solvent and the ability to form eutectics.

The complete reversibility of the variation in the e.s.r. and n.m.r. spectra with temperature shows that the state of frozen multicomponent systems obtained with rates of cooling < 100 deg min^{-1} is close to thermodynamic equilibrium. Hence the volume V_L of microregions of high molecular mobility will be determined by the equation of state of the system. This volume decreases with fall in temperature: i.e. $\partial V_L/\partial T > 0$. To each temperature corresponds a microphase volume in which chemical reaction will occur (if its components are able to interact). When the drop in temperature is sufficient, reactions will cease owing to the increase in viscosity, the decrease in molecular mobility, and the Arrhenius law.

Fig. 4 shows as example the variation in the volume of the liquid microphase during the reaction of triethylamine with iodomethane in frozen benzene. The initial volume of the specimen is $V_0 = 0.36$ ml. Increasing extent of reaction, with decrease in the number of moles, is evidently accompanied by a decrease in V_L. At the same time the total concentration of solutes in the liquid microphase c_L remains constant (Fig. 5). This concentration increases with fall in the temperature, and hardly changes on introduction of the additive. At a given temperature and with a given initial concentration of starting materials, the composition of the liquid microphase depends mainly on the cryoscopic properties of the solvent. The total concentration of solutes in the liquid microphase can be found from the formula

$$c_L = (T_0 - T)/\Delta,$$

where T_0 is the melting point of the solvent and Δ (in deg M^{-1}) is its cryoscopic constant. Table 3 shows quite good agreement between experimental values and those calculated by means of this constant. The result indicates that the state of a slowly frozen multicomponent system is close to thermodynamic equilibrium.

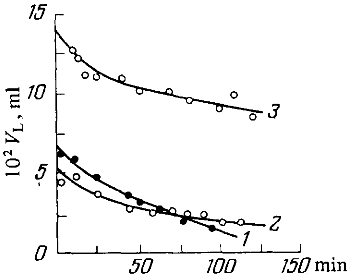


Figure 4. Variation in volume of liquid microphase in reaction of iodomethane with triethylamine (initially 0.2 M) in frozen benzene solutions: 1) at −5°C; 2) at −10°C; 3) with 0.4 M cyclohexane at −5°C; $V_0 = 0.36$ ml.

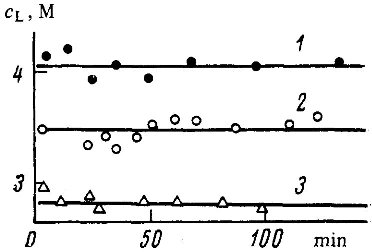


Figure 5. Variation in total solutes concentration c_L in liquid microphase during reaction of triethylamine with iodomethane (both initially 0.2 M) in frozen benzene at: 1) −10°C; 2) −5°C with 0.4 M nitrobenzene; 3) −5°C.

The reason for the formation of a liquid microphase in frozen solutions is that the inclusion of solutes in the crystal lattice of a solid solvent requires a greater quantity of energy than that consumed in the rise in chemical potentials accompanying increase in the concentration of components in the liquid microphase. The origin of microheterogeneities is clear also when eutectics are formed: the concentrating effect accompanying freezing may lead to a composition corresponding to a eutectic mixture. Data on the composition of the liquid microphase obtained by the n.m.r. method show that solutes constitute ~ 20–30% of the total volume of the liquid microphase at temperatures 10–15 deg below the freezing point of the solution.

Table 3. Total concentration of solutes in liquid microphase c_L and observed rate constants k_{exp} in reaction of triethylamine with iodomethane in frozen solutions in benzene, with initial reactant concentrations of 0.2 M.

Additive, 0.4 M	t, °C	$10^4 k_{exp}$, s^{-1}		c_L, M	
		n.m.r.	titration	n.m.r.	calc.
Benzene	−5	1.3±0.7	2.8±0.3	3±1.5	1.8
Nitrobenzene	−5	23±12	13±3	3.5±1.7	1.8
None	−5	4.6±2.3	3.2±0.3	3±1.5	1.8
None	−10	2.7±1.4	2.9±0.3	4±2	2.7

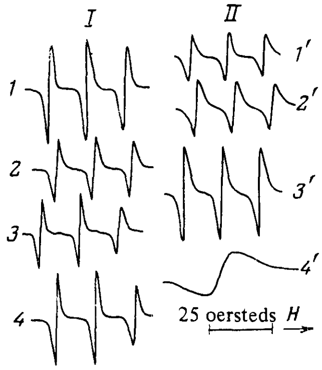


Figure 6. Spectra (e.s.r.) of 10^{-5} M 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl in: I) dioxan (m.p. 11.8°C) at −18°C; II) naphthalene (m.p. 80.1°C) at 25°C in the presence of 0.5 M additions of (correlation time $10^{11}\tau$, s): 1) t-butyl alcohol (13); 2) tetrachloromethane (4.4); 3) water (21); 4) azobenzene (29); 1') dioxan (4); 2') t-butyl alcohol (15); 3') nitrobenzene (26); 4') no addition.

Structural heterogeneity and phase non-uniformity are typical not only of frozen solutions but also of many other multicomponent systems. Fig. 6 shows as example e.s.r. results indicating the existence of a liquid microphase (at 25°C) in solid naphthalene (m.p. 80.1°C) when various additives are introduced[42]. In the absence of an additive the spectrum of the iminoxyl radical in naphthalene is a singlet, which is typical of frozen solutions in other solvents at the temperature of liquid nitrogen. This is converted into a triplet on addition of dioxan, t-butyl alcohol, or nitrobenzene. Thus additive concentrations of 0.5 M or less increase the mobility of the radical by several powers of ten, while the correlation time τ

changes from $< 10^{-5}$–10^{-6} to 4×10^{-11} s. Such a change in mobility is due to the formation, in the matrix of solid naphthalene, of regions of high molecular mobility, which is preserved at a temperature 55 deg below the melting point.

More and more results have appeared recently on molecular mobility in polymers. They indicate that polymer matrices with fillers behave as two-phase systems. The polystyrene–benzene system is characterised over the range −100 to 100°C by two nuclear magnetic spin–spin relaxation times T_2. Protons of benzene are responsible for the "phase" with the longer relaxation time T_{2a}, and protons of the macromolecules for the "phase" with the shorter time T_{2b}.[52] With fall in temperature the population density of the former "phase" diminishes. A sharp decrease in T_{2a} relaxation times is observed in the region of the melting point of benzene. This is evidence of partial crystallisation of benzene and that it in considerable measure determines the composition of this phase. Strictly speaking, the molecular motion of benzene in polystyrene is described by a spectrum of correlation times, and estimates show that the relaxation of benzene molecules in a polystyrene matrix is due mainly to rotational motions[52].

The plasticisation of a polymer by compounds of low molecular weight leads to an increase in molecular mobility. This conclusion is based on the variation in the e.s.r. spectra of radicals and the increase in their rate of conversion[53-55].

Interesting results have been obtained on the behaviour of liquid inclusions in potassium chloride crystals in the field of a temperature gradient[56]. The rate of movement depends on the size of the inclusions and on the applied temperature gradient.

The structure of solid multicomponent systems obtained from the liquid state depends significantly on the setting conditions, primarily on the rate of cooling. Such experiments have been made mainly on alloys. Rates of $\sim 10^3$–10^7 deg s^{-1} lead to extension of the range of solid solutions and a considerable decrease in the liquation of impurity elements, ultimately yielding a homogeneous alloy. Metastable phases and amorphous structures can be obtained with the above rates of cooling[57].

Little if any study has been made of the influence of rate of cooling on the structure of frozen organic-solvent solutions. The thermodynamic disequilibrium of the resulting systems can reasonably be expected to increase with the rate of freezing, which would influence significantly the kinetics of reactions occurring in them. The composition of supersaturated solid solutions formed in the *p*-chloronitrobenzene–*p*-bromonitrobenzene system depends on the rate of crystal growth[58].

It has recently been established that structural inhomogeneity is characteristic not only of crystallising but also of vitrifying systems, e.g. inorganic glasses[59].

Thus available experimental results indicate that multicomponent systems formed from the liquid state with fall in temperature possess both structural and phase heterogeneity. Such systems contain phases differing in composition, physicochemical properties, and degree of molecular mobility.

V. STRUCTURAL–KINETIC MODEL

The phase constitution of multicomponent systems has been examined, and kinetic data on chemical reactions have been obtained for the first time, directly in frozen solutions by application of the e.s.r. and n.m.r. methods. The former has been used to study a reaction involving a stable iminoxyl radical, 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl, and the latter to investigate the Menshutkin reaction[44]. Microwave spectrometry has permitted simultaneous observation of the phase state of the system and the kinetics of the reaction, as well as elimination of the possible effect of thawing, which occurs when specimens are analysed by other methods. Comparison of results obtained by different methods has in turn yielded necessary information on the role of freezing–unfreezing processes. Values obtained by different methods showed good mutual agreement (Table 3). Thus the phase transition connected with thawing out and the method of freezing have hardly any effect on kinetic results for spontaneous chemical reactions.

Let us consider the requirements that should be taken into account in any model intended to describe reactions in frozen solutions. The fundamental kinetic laws discussed in Section III are observed with chemical processes of the most diverse types. Hence the proposed model should be generally applicable and be based on principles taking into account the physicochemical properties common to all frozen systems. On the other hand, the chemical specificity of each individual process should appear in the model.

No-one has hitherto attempted to consider together reactions involving active species (e.g. radicals stabilised in matrices at low temperatures by the action of various types of radiation) and spontaneous chemical reactions occurring in solid matrices. In the Reviewers' opinion these kinetically dissimilar processes are actually most closely interconnected, and form the basis for the same general rules.

Our results on the kinetics of chemical reactions in frozen solutions and their phase condition suggest a structural–kinetic model for chemical reactions in solid matrices[44]. Frozen multicomponent systems have been shown to be heterogeneous with respect to phase. To a first approximation they can be imagined to consist of regions differing in composition and hence with different physicochemical properties. Solutes are preferentially concentrated in some regions, and the solvent is concentrated in others.

Phase heterogeneity may arise also by the action of various types of radiation and other physical agents. Even monocrystalline specimens become inhomogeneous under the influence of γ-rays, with maximum heterogeneity in the vicinity of active species stabilised at low temperatures. We can thus speak of the amorphisation of structure around stabilised radicals.

The actual occurrence of chemical reactions in solid matrices is made possible by the emerging phase heterogeneity (under the influence of freezing, radiation, or some other factor). This brings together the reactants, and thereby satisfies an important condition for reaction to occur. Thus chemical reaction takes place in certain regions of a frozen system. Molecular mobility varies significantly within a region, and shows differences in temperature variation in regions differing in composition. Study by e.s.r. and n.m.r. of the phase condition of frozen binary and ternary systems has shown that the freezing of solutions (in the usual solvents) of substances differing in chemical nature concentrates the latter in regions of enhanced molecular mobility. Over a wide temperature range, extending several tens of degrees below the freezing point, this is closely similar to the mobility in the liquid phase. To a first approximation these regions can be regarded as a liquid microphase located in a solid matrix.

The kinetics of chemical reactions in frozen systems can be explained on the basis of certain fundamental principles. (i) Multicomponent systems are characterised by structural and phase inhomogeneity. The components are non-uniformly distributed in a matrix of the main substance. (ii) Phases having different degrees of molecular mobility coexist over a wide range of conditions. The molecular mobility of reactants in frozen systems over a wide temperature range is closely similar to the mobility in a liquid phase. (iii) Freezing is accompanied by a change in the physicochemical properties of the system, which differ significantly for different phases and cannot be obtained simply by extrapolating data for a homogeneous system. It must especially be noted that, even if the totality of microregions in which reaction mainly occurs are regarded as a liquid microphase, this differs markedly in physicochemical properties from the initial liquid solution and even from its supercooled state if the latter could be obtained.

The frozen system may not in general be necessarily in thermodynamic equilibrium. The function describing its true phase condition can then be found only experimentally. Yet solution of the main kinetic problem—to find the law governing the variation of reactant concentrations with time—is impossible in analytical form without knowledge of this function. Two limiting régimes, corresponding to two possible structural states of the system, can be distinguished for chemical reactions.

Firstly, reaction cannot occur to an appreciable extent during transition of the system from liquid to frozen states with a rate of cooling not exceeding 100 deg min^{-1}, which is frequently the case according to the experimental results. The phase condition of the system is then at or close to thermodynamic equilibrium. Such a régime may be termed *kinetic*. The condition $v < w_{12}$ then holds, where v is the rate of chemical reaction, e.g. in the liquid phase at the melting point, and w_{12} the rate of transition of the system from the phase state at temperature t_1 (at or above the melting point) to the state at temperature t_2 (below the melting point).

The second group of conditions, which we may term a *relaxation régime*, will apply to rapid reactions, when $v > w_{12}$, with rapid quenching of the system, e.g. rates of cooling of $\sim 10^3 - 10^7$ deg s^{-1}. The process will then be governed by the rate of the phase transition. It is especially significant that, with high rates of cooling, the state will not correspond to thermodynamic equilibrium. Transition to a non-equilibrium state may be produced also by other factors, e.g. radiation. The great majority of reactions involving stabilised radicals and other active species in solids occur under a relaxation régime, which, in the Reviewers' opinion, is responsible for the appearance of several unusual features, in particular stepwise recombination.

Formulae for reaction kinetics in frozen systems can be obtained from a combined examination of the equation of state of the system, the equation of material balance describing the distribution of components in individual phases, and kinetic equations defining specific reaction rates in each phase.

Examining the origin of equations for describing reactions occurring under a kinetic régime[44,60-64], we note that experiment shows that the system is then almost in thermodynamic equilibrium, and the unknown equation of state for the frozen system can be replaced by two principles soundly based on experiment. Freezing may be supposed to involve formation of a two-phase system, in which the reaction velocity is $v = v_L + v_S$, where v_L and v_S are the rates in the liquid microphase and in the solid phase respectively. With complete transfer of solutes to the liquid microphase we can ignore v_S, while the great molecular mobility of the reactants allows us to use for v_L the kinetic formula for the rate of a reaction in an ordinary liquid phase, taking into account the changes in temperature and in physicochemical properties accompanying freezing.

The Reviewers and their coworkers have obtained kinetic equations for reactions taking place under a kinetic régime[28,44,61,65]. For the rate of reaction in the liquid microphase of a frozen solution we can write

$$v_L = k^0 \cdot \exp(-E/RT) \cdot \prod_j c_{jL}^{n_j} \tag{1}$$

where E is the activation energy of the reaction determined in the liquid phase, k^0 the pre-exponential factor, T the temperature of the experiment, c_{jL} the concentration of the jth reactant in the liquid microphase, in contrast to its concentration c_j in the unfrozen solution, and n_j the order of the reaction with respect to this reactant. We suppose that a specimen of volume V is frozen, in which the total concentration of all solutes (reactants, catalyst, additives, etc.) is $\sum_i c_i$. We suppose also that the frozen solution at temperature T contains a liquid microphase of volume V_L with a total concentration of solutes of $\sum_i c_{iL}$. Provided that the solutes become entirely concentrated in the liquid microphase on freezing, the material-balance equation is

$$V \cdot \sum_i c_i = V_L \cdot \sum_i c_{iL}. \tag{2}$$

Since the experimental reaction velocity v_{exp} is determined for the whole unfrozen specimen of volume V, the material-balance equation with respect to rates becomes

$$v_{\text{exp}} V = v_L V_L. \tag{3}$$

We introduce the concept of a concentrating factor β_i, the ratio of the concentration of the ith component in the liquid microphase of the frozen solution to its concentration in the unfrozen solution. When such concentrating is complete, β_i is the ratio of the volumes of the unfrozen solution and of the liquid microphase. From (2) and (3) we have

$$\beta_i = \sum_i c_{iL} \Big/ \sum_i c_i = V/V_L = v_L/v_{\text{exp}} \tag{4}$$

or

$$\sum_i c_{iL} = \beta_i \cdot \sum_i c_i \quad \text{and} \quad v_{\text{exp}} = v_L/\beta_i. \tag{5}$$

If the equation of state of the system is not known, experimental results show that $\sum_i c_{iL}$ can be determined by means of the relation

$$T_0 - T = \Delta \cdot \sum_i c_{iL}, \tag{6}$$

where T_0 is the melting point of the solvent and Δ its cryoscopic constant. Combining (5) and (6), we obtain

$$\beta_i = \frac{T_0 - T}{\Delta \cdot \sum_i c_i} \quad \text{and} \quad v_{\text{exp}} = v_L \frac{\Delta \cdot \sum_i c_i}{T_0 - T}. \tag{7}$$

From (1) and (7) we find that the experimental reaction velocity in the frozen solution is given by

$$v_{\exp} = k^{0} \cdot \exp(-E/RT) \cdot \left[\frac{T_0 - T}{\Delta \cdot \sum_i c_i}\right]^{\left(\sum_j n_j - 1\right)} \cdot \prod_j c_j^{n_j}. \tag{8}$$

The formula for the rate of a reaction in a frozen solution can be written as the product of the reactant concentrations and a factor that behaves formally as a rate constant:

$$v_{\exp} = k_{\exp} \cdot \prod_j c_j^{n_j}, \tag{9}$$

where

$$k_{\exp} = k^{0} \cdot \exp(-E/RT) \cdot \left[(T_0 - T)/\Delta \cdot \sum_i c_i\right]^{\left(\sum_j n_j - 1\right)}, \tag{10}$$

i.e. $k_{\exp}$ is the product of the usual reaction rate constant at temperature T and the concentrating factor β_i raised to a power depending on the total reaction order $\sum_j n_j$. The concentrating factor depends on the properties of the solvent (its melting point and cryoscopic constant), the experimental temperature, and the total concentration of all the solutes $\sum_i c_i$. The concentrating factor and temperature T will be larger the greater is the difference $T_0 - T$ and the smaller are Δ and $\sum_i c_i$. The inverse proportion relating β_i with Δ and $\sum_i c_i$ has a clear physical explanation. The equilibrium state between the liquid solution and the frozen solvent at temperature T corresponds to a definite concentration of solutes, which is inversely proportional to the cryoscopic constant of the solvent. Thus the lower had been the concentration of solutes in the liquid solution $\sum_i c_i$ the more strongly should they be concentrated for the freezing point of the solvent to be depressed by $T_0 - T$.

The reactants, reaction products, catalysts, and other additives contribute to $\sum_i c_i$. In the simplest case the concentration of an inert additive in the reaction mixture c_a far exceeds the sum of the concentrations of the remaining components (other than the solvent):

$$c_a \gg \sum_i c_i. \tag{11}$$

We can then write

$$\sum_i c_i \approx c_a, \quad \sum_i c_{iL} \approx c_{aL} \tag{12}$$

$$\beta_i = \beta_a = \frac{T_0 - T}{\Delta \cdot c_a}, \tag{13}$$

i.e. the ratio of the volumes of unfrozen solution and liquid microphase, and hence the degree to which the reactants become concentrated, depend on the concentration of the inert additive.

Table 4 lists formulae for the rate constants $k_{\exp}$ of various types of reactions occurring in frozen solutions in the presence and in the absence of an additive. The experimental rate constants determined in frozen solutions containing an additive are seen to be independent of the reactant concentrations and to differ from the constants for the same reaction in the liquid phase by the $(\sum_j n_j - 1)$th power of the factor $\beta = (T_0 - T)/\Delta c_a$. In the absence of an additive, however, values of $k_{\exp}$ for reactions involving either a decrease of an increase in the number of moles depend on the instantaneous concentration of the reactants and are a function of the extent of reaction. The explanation is that, with reactions involving a change in the number of moles, the volume of the liquid microphase will change during the reaction in order to satisfy the condition of phase equilibrium. This requirement is equivalent to the condition

$$\sum_i c_{iL} = \text{const} \tag{14}$$

in the given solvent at temperature T.

Table 4. Values of factor γ in the formula

$$k_{\exp} = k^{0} \cdot \exp(-E/RT) \cdot \frac{T_0 \cdot T}{\Delta} \cdot \gamma$$

for the experimental rate constants of various types of reactions*.

Type of reaction	Factor
$A+B \longrightarrow C$	$([A]+[B]_0)^{-1}$
$A+B \longrightarrow C+D$	$([A]_0+[B]_0)^{-1}$
$A+B \longrightarrow C+D+E$	$(2[A]_0+[B]_0-[A])^{-1}$
$A+B+K \longrightarrow C+K$	$\dfrac{T_0-T}{\Delta \cdot ([A]+[B]_0+[K])^2}$
$A+B+K \longrightarrow C+D+K$	$\dfrac{T_0-T}{\Delta \cdot ([A]_0+[B]_0+[K])^2}$
$A+B+K \longrightarrow C+D+E+K$	$\dfrac{T_0-T}{\Delta \cdot (2[A]_0+[B]_0+[K]-[A])^2}$

* With $\sum_i c_i \simeq c_a$ we have $k_{\exp} = k^{0} \cdot \exp(-E/RT) \cdot \left(\frac{T_0-T}{\Delta \cdot c_a}\right)^n$, where $n = 2$ for bimolecular reactions in the presence of a catalyst (K), and $n = 1$ for uncatalysed reactions.

In order to obtain analytical expressions for the time variation of the concentrations of reactants or reaction products, the corresponding differential kinetic equations must be integrated. Considering as example the reaction A + B → C + D + E occurring in a frozen solution in the presence of an additive of concentration c_a, which does not appear in the stoichiometric equation, we write for the experimental rate constant

$$v_{\exp} = \frac{d[C]}{dt} = k_{\exp}[A] \cdot [B], \tag{15}$$

where (Table 4)

$$k_{\exp} = k_0 \cdot \exp(-E/RT) \cdot \frac{T_0 - T}{\Delta \cdot c_a}. \tag{16}$$

The instantaneous concentrations [A], [B], and [C] during the reaction are related to the initial concentrations $[A]_0$ and $[B]_0$ by the formulae

$$[A] = [A]_0 - [C] \text{ and } [B] = [B]_0 - [C]. \tag{17}$$

Substituting (17) in (15), we obtain

$$\frac{d[C]}{dt} = k_{\exp}([A]_0 - [C])([B]_0 - [C]). \tag{18}$$

The variables in this differential equation are separated:

$$\frac{\mathrm{d}[\mathrm{C}]}{([\mathrm{A}]_0-[\mathrm{C}])([\mathrm{B}]_0-[\mathrm{C}])}=k_{\exp}\cdot \mathrm{d}t. \tag{19}$$

Rearrangement of the left-hand side yields

$$\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\cdot\left(\frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{B}]_0-[\mathrm{C}]}-\frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{A}]_0-[\mathrm{C}]}\right)=k_{\exp}\cdot \mathrm{d}t \tag{20}$$

integration of which, with the initial condition $[\mathrm{C}]=0$ at $t=0$, gives

$$[\mathrm{C}]=\frac{[\mathrm{A}]_0[\mathrm{B}]_0\{1-\exp[k_{\exp}\cdot t([\mathrm{A}]_0-[\mathrm{B}]_0)]\}}{[\mathrm{B}]_0-[\mathrm{A}]_0\cdot\exp[k_{\exp}\cdot t([\mathrm{A}]_0-[\mathrm{B}]_0)]}, \tag{21}$$

It is evident that Eqn. (21), describing the rate curve representing accumulation of the reaction product C, is identical in form with the equation for the liquid phase, but with the usual rate constant $k=k_0\exp(-E/RT)$ replaced by $k_{\exp}$ (Eqn. 16).

For the same reaction taking place in a frozen solution containing no additive the rate is given by Eqn. (15) but with $k_{\exp}$ dependent on the instantaneous concentration of one of the starting materials (Table 4):

$$k_{\exp}=k_0\cdot\exp(-E/RT)\cdot\frac{T_0-T}{\Delta\cdot(2[\mathrm{A}]_0+[\mathrm{B}]_0-[\mathrm{A}])}. \tag{22}$$

Since formulae (17) still hold, we can write for the reaction velocity the differential equation

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}=k_0\cdot\exp(-E/RT)\cdot\frac{T_0-T}{\Delta}\cdot\frac{([\mathrm{A}]_0-[\mathrm{C}])([\mathrm{B}]_0-[\mathrm{C}])}{[\mathrm{A}]_0+[\mathrm{B}]_0+[\mathrm{C}]}, \tag{23}$$

or

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}=k\frac{([\mathrm{A}]_0-[\mathrm{C}])([\mathrm{B}]_0-[\mathrm{C}])}{[\mathrm{A}]_0+[\mathrm{B}]_0+[\mathrm{C}]}, \tag{24}$$

where

$$k=k_0\cdot\exp(-E/RT)\cdot\frac{T_0-T}{\Delta}.$$

After separation of variables Eqn. (24) becomes

$$\mathrm{d}[\mathrm{C}]\frac{[\mathrm{A}]_0+[\mathrm{B}]_0+[\mathrm{C}]}{([\mathrm{A}]_0-[\mathrm{C}])([\mathrm{B}]_0-[\mathrm{C}])}=k\cdot\mathrm{d}t. \tag{25}$$

Integration of this equation, after the requisite rearrangements and with the initial condition $[\mathrm{C}]=0$ at $t=0$ will give

$$\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\cdot\left[(2[\mathrm{A}]_0+[\mathrm{B}]_0)\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{A}]_0}\right)-[\mathrm{A}]_0\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{B}]_0}\right)-2[\mathrm{C}]\right]=kt. \tag{26}$$

Analytical expressions can similarly be obtained for the time dependence of the concentration [C] of the product of other types of bimolecular reactions in frozen solutions. Table 5 shows that it is only when the solution contains an additive or the number of moles remains unchanged that the rate curves of reactions in frozen solutions are described by the same equations as in the liquid phase but with different constants. The experimental rate constants are then proportional to the concentrating factor, and therefore depend either on the sum of the initial concentrations of the starting materials or on the concentration of the additive.

In the absence of an additive an explicit equation for the rate of accumulation of a product can in general ($[\mathrm{A}]_0\neq[\mathrm{B}]_0$) be obtained only for reactions in which the number of moles is maintained. For reactions involving a change in the number of moles formal kinetic equations cannot be used to describe the rate curves in frozen systems. In particular, processing experimental data on the basis of formal equations may lead to errors in determining the order of a reaction.

The model also provides a qualitative explanation and a quantitative description of the observed bell-shaped temperature dependence of reaction velocity (Fig. 1). The physical meaning of such variation is that freezing the solutions and cooling them below the freezing point tends to slow down the reaction in conformity with the Arrhenius law and to accelerate it because of the increase in concentration of the reactants and the change in physicochemical conditions in the liquid microphase: competition between these three effects is responsible for the appearance of a maximum.

Table 5. Analytical formulae for the time dependence of the concentration of a product C of various types of bimolecular reactions (Table 4) occurring in frozen solutions in the absence of an additive*.

Reaction	Formula for [C], where $k_{\exp}=k_0\cdot\exp(-E/RT)\cdot\frac{T_0-T}{\Delta}\cdot\gamma$	γ
$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}$	$\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\left[[\mathrm{B}]_0\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{A}]_0}\right)-[\mathrm{A}]_0\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{B}]_0}\right)\right]=k_{\exp}t$	1
$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}+\mathrm{D}$	$[\mathrm{C}]=\frac{[\mathrm{A}]_0[\mathrm{B}]_0\{1-\exp[k_{\exp}\cdot t([\mathrm{A}]_0-[\mathrm{B}]_0)]\}}{[\mathrm{B}]_0-[\mathrm{A}]_0\cdot\exp[k_{\exp}t([\mathrm{A}]_0-[\mathrm{B}]_0)]}$	$([\mathrm{A}]_0+[\mathrm{B}]_0)^{-1}$
$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}+\mathrm{D}+\mathrm{E}$	$\frac{1}{[\mathrm{A}]_0-[\mathrm{B}]_0}\left[(2[\mathrm{A}]_0+[\mathrm{B}]_0)\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{A}_0]}\right)-(2[\mathrm{B}]_0+[\mathrm{A}])\cdot\ln\left(1-\frac{[\mathrm{C}]}{[\mathrm{B}]_0}\right)\right]=k_{\exp}t$	1

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*In the presence of an additive ($\sum_i c_i\simeq c_a$) the concentration [C] is given for all reactions by the formula for the reaction $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{C}+\mathrm{D}$, with $\gamma=1/c_a$.

In order to find the extrema in the general temperature dependence of reaction velocity in a frozen solution we differentiate Eqn. (8) with respect to temperature:

$$\frac{\partial v_{\exp}}{\partial T}=k^0\cdot\exp(-E/RT)\cdot\left(\prod_j c_j^{n_j}\right)\cdot\left(\frac{1}{\Delta\cdot\sum_i c_i}\right)^{\left(\sum_j n_j-1\right)}\cdot(T_0-T)^{\left(\sum_j n_j-1\right)}\cdot\left[\frac{E}{RT^2}-\frac{\sum_j n_j-1}{T_0-T}\right] \tag{27}$$

and equate this $\partial v_{\exp}/\partial T$ to zero. Formula (27) shows that this is possible only if

$$(T_0-T)^{\left(\sum_j n_j-1\right)}\cdot\left[\frac{E}{RT^2}-\frac{\sum_j n_j-1}{T_0-T}\right]=0. \tag{28}$$

This can occur in several cases:

$$\text{(a)}\quad (T_0-T)\left(\sum_j n_j-1\right)=0,$$

i.e. the extremal point T^* corresponds to the melting point of the solvent, a case which is of no special interest and therefore will not be examined;

$$\text{(b)}\quad \frac{E}{RT^2}-\frac{\sum_j n_j-1}{T_0-T}=0 \tag{29}$$

in which there are several possibilities. When the aggregate order of the reaction is unity (i.e. $\sum_j n_j = 1$), it follows from (29) that the presence of an extremum requires that $E/RT^2 = 0$. If $E \neq 0$, this condition is not realised at any temperature: i.e. the temperature dependence of $v_{\exp}$ for first-order reactions is devoid of extrema. With $\sum_j n_j = 1$ we have

$$\frac{\partial v_{\exp}}{\partial T} \approx \frac{E}{RT^2} \cdot \exp(-E/RT) > 0. \qquad (30)$$

Hence $v_{\exp}$ decreases as the temperature falls, and no acceleration of the reaction should be observed when solutions are frozen. Nor is condition (29) realised at any temperature if $\sum_j n_j < 1$. This means that the temperature dependence of $v_{\exp}$ does not pass through extrema, and the reaction velocity decreases with fall in temperature.

The total reaction order must exceed unity, i.e. $\sum_j n_j - 1 > 0$, for extrema to be present. The extremal point is then found by solving Eqn. (29) for temperature:

$$T^* = \left\{ \frac{E^2}{4R^2\left[\left(\sum_j n_j\right) - 1\right]^2} + \frac{E \cdot T_0}{R\left[\left(\sum_j n_j\right) - 1\right]} \right\}^{1/2} - \frac{E}{2\left[\left(\sum_j n_j\right) - 1\right]} \cdot \qquad (31)$$

This formula shows that the temperature T^* depends on the aggregate order of the reaction, and falls as the order increases. It depends also on the freezing point of the solvent and the activation energy in the liquid phase. Thus if several parallel reactions, having different orders or differing markedly in activation energy, take place in a system, each will occur at a maximum rate at a particular temperature of the frozen solution. This implies that, by conducting the process in the frozen solution at a chosen temperature, we are able to accelerate selectively one or more reactions occurring in parallel in the system.

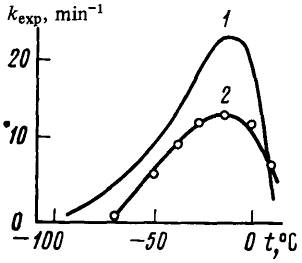

Figure 7. Temperature dependence of rate constant for the oxidation of hydrazobenzene by 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl in frozen dioxan: 1) calculated curve; 2) experimental curve.

The occurrence in frozen solutions of the maximum reaction velocity predicted by the model indicates that these reactions have a negative temperature coefficient, i.e. an effective activation energy less than zero, over the temperature range $T_0 - T^*$. A formula can be obtained for the effective activation energy of a reaction in a frozen solution by differentiating with respect to the reciprocal of the temperature the logarithm of the experimental rate constant (Eqn. 10):

$$E_{\text{eff}} = -R\frac{d \ln k_{\exp}}{d(1/T)} = E - \left[\left(\sum_j n_j\right) - 1\right]\frac{RT^2}{T_0 - T}. \qquad (32)$$

This expression (32) indicates that, when the solution freezes, the activation energy of the reaction changes sign, and remains negative down to the temperature T^*, when it vanishes; after this E_{eff} again becomes positive.

VI. SOME APPLICATIONS OF THE MODEL

Experimental results are well reproduced by the equations obtained[42-44,60-66]. As example Fig. 7 compares the experimental temperature dependence with the calculated relation for the rate constant in the oxidation of hydrazobenzene by 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl. Good qualitative agreement is evident, and at several temperatures nearly identical calculated and experimental values.

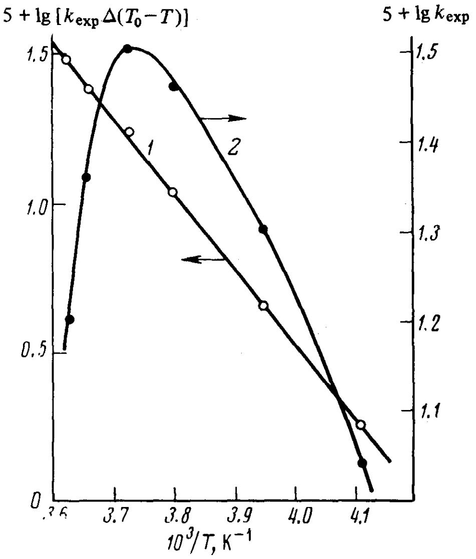

Figure 8. Influence of the reciprocal of the temperature in the Menshutkin reaction in frozen benzene on: 1) $\lg[k_{\exp}\Delta(T_0 - T)]$; 2) $\lg k_{\exp}$.

Results plotted in conformity with the Arrhenius equation do not lie on a straight line (Fig. 8). Linearisation can be effected by the use of coordinates allowing for transition of the system into the frozen state. Table 6 shows good agreement between the values thus obtained for the activation energies of reactions in frozen solutions and the corresponding activation energies in the liquid phase. Good agreement is evident also between calculated and experimental temperatures for maximum reaction velocity.

Let us consider briefly the possibilities of the structural–kinetic model for describing the kinetics of reactions occurring under a relaxation régime[67]. Stepwise recombination in the destruction of radicals stabilised in solids is especially interesting from this point of view. It is observed in systems of the most diverse chemical nature, including polymers[68–79]. The recombination of peroxy-radicals obtained by the photolysis of frozen aqueous hydrogen peroxide was one of the first examples of the stepwise recombination of radicals and the special role of phase transitions in effecting chemical reactions at low temperatures[9,71]. Fundamental kinetic laws were formulated[73] for the stepwise recombination of radicals.

Table 6. Calculated and experimental temperatures of maximum reaction velocity $t_{\mathrm{max}}^{\mathrm{calc}*}$ and $t_{\mathrm{max}}^{\mathrm{exp}}$, with activation energies in the liquid phase and in frozen solutions E and E_{fr} (R = 4-hydroxy-2,2,6,6-tetramethylpiperidinooxyl).

Solvent	E, kcal mole^{-1}	E_{fr}, kcal mole^{-1}	$t_{\mathrm{max}}^{\mathrm{calc}}$, °C	$t_{\mathrm{max}}^{\mathrm{exp}}$, °C
		$CH_3I + (C_2H_5)_3N$		
Benzene	9.4±1.0	11.4	−9±2	−5
Nitrobenzene	9.7±1.0	11.8	−8±2	−5
Dioxan	6.8±1.0	9.6	−9±2	−6
Water	20.3±1.0	23.2	−8±2	−8
		$R + C_{12}H_{12}N_2$		
Dioxan	6±1.0	6.5	−14±2	−20
		$R + C_6H_8O_6$		
Water	12±2	17	−10.5±3	−10

*Deviations calculated on the basis of the error adopted for E in ±1.0 kcal mole^{-1}.

The temperature dependence of the fraction of stabilised radicals (the "annealing" curve) is not in general linear. It probably represents the temperature dependence of the molecular mobility necessary for the destruction of radicals. The curve for radicals in adipic acid is almost linear under normal pressure, but at high pressures it becomes a more complicated function of temperature[74]. The thermal stability of radicals increases with increase in pressure, which is consistent with a decrease in molecular mobility with rise in pressure. It depends on the method of preparing the specimen and the mode of generation of the radicals (e.g. the type of radiation).

Various ideas and hypotheses have been put forward on the mechanism of the destruction of radicals in solids[68,70,73,75–78]. A polychromatic kinetic model of radical reactions in solids has been proposed[69] for the quantitative explanation of recombination. It has recently been suggested[79,80] that the free volume plays a part in the kinetics of radical destruction. Existing models do not explain all the observed regularities, and many concepts based on them are formally kinetic in character.

The concepts underlying the structural–kinetic model[44] also provide a qualitative description of the main kinetic features of the reactions of active species in solids[67]. They lead to a kinetic equation for the stepwise recombination of radicals, including the initial rapid destruction[67]. Such an approach will explain many aspects of solid-phase polymerisation and reactions in polymer systems. The laws governing photochemical reactions in solids can be explained by the same ideas. Solid-phase processes are characterised by a disproportionately large effect of small additions. Yields of products in photochemical and radiation-chemical reactions in multicomponent systems are usually non-additive and have abnormal values, while the rates of the processes are high. Tunnelling and the transfer of excitation and the free valency are often postulated to explain these features.

The concepts underlying the structural–kinetic model show, in the Reviewers' opinion, the absolute necessity of taking into account the fact[67] that, in regions surrounding already formed stabilised radicals, the medium possesses significantly different properties from those of the original matrix before exposure (this possibility had been pointed out by Semenov[2]). The yield of radicals and other species in this new structure will differ from their yield in regions of the solid not yet damaged by radiation. Thus differences in the mechanism and the efficiency of processes occurring in these regions of the solid must be taken into account. In particular, it must be expected that the yield of radicals will increase (because of the diminished cage effect) in radiation-damaged regions, i.e. where stabilised radicals are already present. Such an approach provides an explanation of the enhanced probability of formation of radicals near already existing radicals, and hence the increase in their rate of destruction with increase in dosage. The suggested mechanism may explain the high energy yield of the destruction of radicals, the low apparent activation energies, and the close similarity of radical-destruction rate constants in different substances[68]. The same mechanism should lead to a change in the type of dependence of the rate of accumulation of active particles on the dose. The formation of considerable quantities of radical-recombination products becomes understandable.

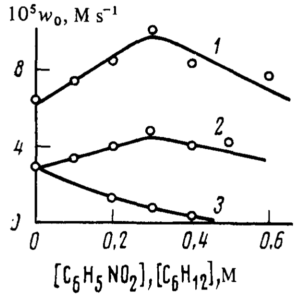

Figure 9. Effect of additives on rate w_0 of reaction of triethylamine with iodomethane in frozen solutions in: 1) dioxan at −8°C with additions of nitrobenzene (initial reactant concentration 0.11 M); 2) benzene at −5°C with additions of nitrobenzene (initial reactant concentrations 0.15 M); 3) as (2) but with added cyclohexane.

The existence in frozen solid matrices of regions of phase heterogeneity with a high mobility of interacting species would permit a physically clear interpretation of many kinetic features of chemical reactions in frozen solutions. These concepts have permitted a comparison of experimental and calculated values, as well as the prediction and detection of several new phenomena.

The rates of chemical reactions in frozen solutions are controlled by adding to the reaction mixture substances that are not involved in the process described by the stoichiometric equation. According to the model described in Section V, additions of inert substances should increase the volume of the liquid microphase and diminish the reactant concentrations. Non-polar additives behave in this way. Fig. 9 shows that polar additives have a dual effect: with low concentrations of the polar nitrobenzene reaction rates in the frozen solution are higher than in the solution without additive, because of the increase in polarity; with increase in the nitrobenzene concentration the dilution of the reactants in the liquid microphase increases because of the change in volume of this phase. The combined action of these two opposite effects leads to the appearance of maxima in the dependence of the initial reaction velocity on the additive concentration. The influence of the dielectric constant on reactions in frozen solutions has been discussed in detail[61,62].

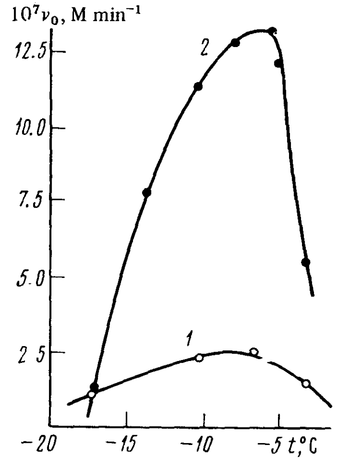

Figure 10. Temperature dependence of rate of oxidation of 4-hydroxy-2,3-dimethyl-1-naphthyl dihydrogen phosphate (2.5×10^{-5} M) by hydrogen peroxide (3.5×10^{-5} M) at pH 7.0 (0.1 M phosphate buffer) in ice in the presence of peroxidase (1.5×10^{-9} M): 1) individual oxidation; 2) in the presence of *p*-hydroxyphenyl dimethyl phosphate (1.4×10^{-5} M) as activator.

To describe the effect of additives we can formulate the general rule that the reaction is retarded in the frozen solution if the rate of the process in the liquid additive as solvent is lower than its rate in the solvent used in the experiment; an additive may either lower or raise the rate in a frozen solution if the rate in the liquid additive as solvent is greater than in the solvent to be frozen. Thus the rate of a process in a frozen solution can be regulated by additions of substances that are not involved in the stoichiometric equation and do not influence the kinetics of the reaction in the liquid phase. It is important to stress that the quantities of additives do not exceed 5% by volume, and are comparable with the concentrations of the reactants.

The structural–kinetic model suggests special effects produced by freezing for reactions having a complicated mechanism and involving a large number of species. Such processes include many biochemical and especially enzymic reactions. The spatially close approach of the reactants should lead to marked acceleration of such reactions, but diffusion hindrance would lead to sharp retardation.

The above suggestions have found some confirmation in the investigation of the two-substrate oxidation of quinol phosphates by hydrogen peroxide in the presence of peroxidase in frozen solutions[81]. Substrate–substrate activation is observed for this reaction in the liquid phase[82]: when two different compounds are oxidised together, the presence of one substrate activates the oxidation of the other. Only one of the substrates is oxidised, while the activator is not consumed until considerable degrees of conversion have been reached. Activation is a result of the concerted oxidation of substrates differing in reactivity at the stages of formation and interaction of radicals.

Fig. 10 illustrates the temperature dependence of the rate of two-substrate oxidation in ice. The presence of the activator is seen to increase the rate of oxidation of 4-hydroxy-1-naphthyl phosphate. The phenomenon of substrate–substrate activation in ice confirms the main assumptions of the structural–kinetic model, and shows that both freezing and the introduction of an additive—the other substrate—enable the rate of the process to be controlled and the efficiency of the enzyme to be enhanced.

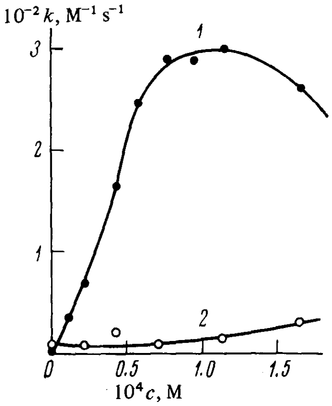

Figure 11. Dependence of rate constant of reaction of glycylphenylalanine (3.3×10^{-4} M) with fluoro-2,4-dinitrobenzene (3.3×10^{-4} M) on concentration of hexadecyltrimethylammonium bromide *c* at pH 7.25 (0.1 M phosphate buffer) in: 1) ice at −10°C; liquid phase at 20°C.

The concepts of the phase heterogeneity and the special properties of frozen solutions have enabled additional structure formation in ice to be predicted and detected. The example of nucleophilic substitution between glycylphenylalanine and fluoro-2,4-dinitrobenzene in ice has revealed a phenomenon resembling micellar catalysis in the liquid phase[83]. Comparison of the results plotted in Fig. 11 show that hexadecyltrimethylammonium bromide becomes active in ice at concentrations that do not influence the reaction in the liquid phase. It is interesting that in the latter the main reaction is accompanied by hydrolysis of fluoro-2,4-dinitrobenzene, whereas transition of the system to the frozen state changes the direction of reaction: freezing accelerates selectively the condensation and suppresses the hydrolysis.

The above examples lead to the important conclusion that the freezing of a system is an effective new method for controlling the rate and the mechanism of a chemical reaction.

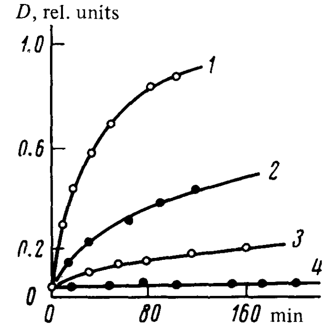

Figure 12. Rate curves for the accumulation of azobenzene in the oxidation of hydrazobenzene (initially 1.1 × 10^{-4} M) in the presence of 0.01 M ethanol in dioxan solution by: 1) iminoxyl radical in frozen solution at −5°C; 2) iminoxyl radical in liquid solution at 20°C; 3) air in liquid solution at 20°C; 4) air in frozen solution at −5°C.

The structural–kinetic model of reactions in multicomponent systems has led to the prediction and the detection of kinetic selection[28], the essence of which is that, among several parallel reactions in a liquid phase, only one is accelerated preferentially when the system passes into the frozen state. We consider as example two parallel bimolecular reactions

$$A+B \xrightarrow{k_1} E+F \tag{I}$$

$$C+D \xrightarrow{k_2} K+H \quad . \tag{II}$$

If D is present in excess, reaction (II) can be regarded as unimolecular and written

$$C \xrightarrow{k_3} K+H, \tag{III}$$

where $k_3 = k_2[D]$. From Eqn. (8) the rates of reactions (I) and (III) in the frozen solution are

$$v_1 = k_{1\,\mathrm{exp}}[A][B] = \frac{T_0-T}{\Delta\cdot([A]_0+[B]_0)}\cdot k_{01}\cdot\exp(-E_1/RT) \tag{33}$$

$$v_3 = k_{3\,\mathrm{exp}}[C] = k_{02}\cdot\exp(-E_2/RT)\cdot[D][C] \quad . \tag{34}$$

The ratio of the rates at temperature T is

$$\frac{v_1}{v_3} = \frac{T_0-T}{\Delta\cdot([A]_0+[B]_0)}\cdot\frac{k_{01}\cdot\exp(-E_1/RT)\cdot[A][B]}{k_{02}\cdot\exp(-E_2/RT)\cdot[C][D]} \quad , \tag{35}$$

The corresponding ratio in the supercooled liquid phase at the same temperature is

$$\frac{v_{1L}}{v_{3L}} = \frac{k_{01}\cdot\exp(-E_1/RT)}{k_{02}\cdot\exp(-E_2/RT)}\cdot\frac{[A][B]}{[C][D]}. \tag{36}$$

Comparison of (35) and (36) shows that the rate ratio varies differently in liquid and frozen solutions. Transition of the system from one phase to the other leads to a difference in rates defined by the relation

$$\frac{v_1/v_3}{v_{1L}/v_{3L}} \simeq \frac{T_0-T}{\Delta\cdot([A]_0+[B]_0)}. \tag{37}$$

Fig. 12 illustrates the effect of freezing on the oxidation of hydrazobenzene by atmospheric oxygen and by the 4-hydroxy-2,2,6,6-tetramethylpiperidino-oxyl radical in dioxan. Calculation for 253 K gives the value 3.6 × 10^4, so that the rate of oxidation by dissolved oxygen has decreased by a factor exceeding 35 000. Yet the rate of oxidation by the radical has accelerated in frozen solutions relative to the liquid phase. A similar pattern is observed in the oxidation of ascorbic acid[28].

One factor affecting the activation of chemical reactions on transition to the frozen state is the concentrating of the reactants. Such effects should be most strongly developed, of course, in reactions involving molecular complexes. Data on the halogenation of alkenes indicates that the phenomenon of a negative temperature coefficient is intensified when the system passes into the solid phase[66]. The combined activation of chemical processes by low temperatures and complex formation is clearly evident in the example of halogenations. Low-temperature reactions in the absence of a solvent (Table 1) have usually been investigated at temperatures at which the reactants exist in the solid phase. The preparation of such specimens may involve the formation of structural and phase discontinuities. Such a possibility is indicated by n.m.r. investigations on chlorine–alkene systems[84]. Thus at low temperatures some common features are exhibited by reactions in binary systems in the absence of a solvent and in multicomponent systems containing a solvent.

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Research on frozen multicomponent systems has shown that the structural and phase inhomogeneity of the specimens has a decisive influence on the kinetics of chemical reactions occurring in such systems. Experimental results indicate that transition of a system from one phase to another is accompanied by a considerable change in physicochemical properties. Even in cases in which structural inclusions can be regarded as a liquid phase, its density, viscosity, dielectric constant, and other physicochemical characteristics cannot be obtained by extrapolating values for the truly liquid systems. These parameters are determined by the properties of the frozen specimen as a single whole.

The situation is further complicated by the absence of a strict definition for most physicochemical parameters at low temperatures and in the solid phase. Hitherto we have known really very little about the true phase condition of multicomponent systems at low temperatures, especially when subject to various radiations and with change in temperature. In the Reviewers' opinion the most fertile approach to the solution of many problems of low-temperature chemistry is to consider not only the specific chemistry of the process but also the effect of the actual phase condition of the whole system.

Only macrokinetic rules based on the structural–kinetic model have yet been obtained for frozen multicomponent systems. Further investigations are necessary to establish the dependence of the rate constant on the structure and the phase condition of the system, and to determine the quantitative influence of various factors, such as the movement of inclusions, methods of obtaining them, and the role of thermodynamic and kinetic factors in effecting chemical changes in frozen solid matrices. Solution of these problems is of great theoretical and practical interest. Research on chemical and biochemical reactions at low temperatures will enlarge our views on the mechanism of chemical change under extreme conditions, permit new approaches to the control of chemical synthesis, and enable optimum conditions to be predicted for the preservation of medical and biochemical preparations, as well as foodstuffs.

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Problems of Combustion in Chemical Technology and in Metallurgy

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Combustion processes leading to the formation of valuable products of chemical technology and metallurgy—acetylene, carbon black, starting materials for acid manufacture, metal oxides, ferro-alloys, refractory compounds, etc.—are surveyed with emphasis on the possibilities and the advantages of combustion as a technical chemical procedure. Prospects for the widespread utilisation of combustion processes in chemical technology and metallurgy are examined on the basis of specific examples. Certain aspects of the development of combustion theory in connection with technical problems are discussed. A list of 78 references is included.

CONTENTS

I. INTRODUCTION

The term *combustion* is usually applied to a strongly exothermic chemical reaction occurring at temperatures resulting from the evolution of the heat of reaction. Two fundamentally different combustion régimes can be established: in the layered (wave) process reaction occurs in a narrow zone separating the reactants from the heated reaction products and moving spontaneously through the material at a definite speed in the form of a combustion wave; in the homogeneous process the reaction occurs in a combustion chamber to which reactants are continuously supplied and from which reaction products are continuously removed, while reactants and products are mixed. A characteristic feature in both cases is the high temperature arising during the reaction from the liberation of the chemical energy of the initial system, unconnected with an external supply of energy. Other forms of combustion include, for instance, the diffusion combustion of gases, in which the reactants are not mixed but are fed from different sides to a flame front whose position is stabilised in space.

The theoretical foundations were laid during the 1930 to 1940s by the fundamental investigations of Semenov and his school[1-3]. He examined the laws of the evolution and removal of heat in the reacting material[4], and calculated for the first time the critical conditions for thermal explosion. Subsequently Frank-Kamenetskii[5,6] and Todes[7-10] made important advances in the theory of the thermal explosion of gases. The theory of flame propagation was established by Zel'dovich and Frank-Kamenetskii[11]. Zel'dovich worked out the theories of combustion limits[12] and the combustion of unmixed gases[13], and also discussed the thermal conditions of exothermic reactions in a flow-type reaction vessel[14,15]. Several theoretical investigations of thermal explosion, ignition, and the propagation of a combustion wave in a condensed system have been undertaken by the Reviewer[16-20].

Two broad uses of combustion can be distinguished. Firstly the generation of power utilises the heat of reaction and very often, but not always, the energy of the expanding gaseous products. In the second use a product of combustion is itself of interest, as the desired result of a technical process.

The generation of power has been hugely developed and has exerted a strong influence on the theory of combustion. Almost all problems in the theory arose from the utilisation of chemical energy. Combustion theoreticians on their part have made an important contribution to energetics. The joint efforts of scientists and designers have developed such fields as engine manufacture, heat and power engineering, and rocket technology.

The second use has been developed mainly by technical chemists and metallurgists in isolation from combustion theory, and has reduced to working out the technology of individual products. Unfortunately, the extent and the level of investigations have been inadequate, and do not correspond to the great importance of this problem for the national economy.

This Review is an attempt to systematise the main combustion processes employed to obtain useful substances (gaseous and condensed products of chemical industry, metals and alloys, refractory inorganic compounds, etc.), to formulate specific features of combustion as a process of chemical technology, and to discuss certain problems associated with its development. Other aspects of combustion are also of interest to chemical technology and metallurgy, among them security from fire and explosion in chemical industries (the theoretical foundations of safety techniques), the production of technical furnaces burning natural fuels, and the organisation of thermal processes in flames. Here, however, we shall discuss only problems on synthesis, which are the most urgent and the least investigated.

II. MAIN TYPES OF TECHNICAL COMBUSTION PROCESSES

We shall discuss briefly the most widely used technical combustion processes.

1. Combustion of Hydrocarbons

The combustion of hydrocarbons is used in chemical industry to obtain various products (process gas, ethylene and acetylene, carbon black, etc.). Many variants of the process are used, distinguished by the starting material (usually natural gas and air), the concentration ratio of combustible and oxidant, the design of burners or combustion chambers, and methods of removing the required products.

Process gas is manufactured by the combustion of a hydrocarbon according to the equation

$$C_nH_{2n+2} + \frac{n}{2} O_2 = n\,CO + (n+1)\,H_2.$$

The products are in thermodynamic equilibrium, and are used for the synthesis of ammonia and methanol[21].

Acetylene and carbon black are obtained by combustion that is kept incomplete[22-26]. Excess of a hydrocarbon is pyrolysed in the flame formed by burning the major part of the hydrocarbon:

$$C_nH_{2n+2} \to C_2H_4 \to C_2H_2 \to C.$$

This process has been termed *oxidative pyrolysis*. Sometimes different hydrocarbons are used for combustion and pyrolysis, the latter being introduced directly into the flow of combustion products. Acetylene is an intermediate product of pyrolysis. It is therefore obtained by quenching (water is usually sprayed into the reacting mixture). The duration of the pyrolysis stage (which should be optimum) and the intensity of quenching (which should be great) determine the yield of acetylene — the chief index of the efficiency of a particular technical scheme.

Carbon black is the final product of pyrolysis, which is made as complete as possible in manufacture. A specific design feature of the plant is the presence of collectors for the condensed phase (soot collectors). Important characteristics of carbon black are its degree of dispersion and its impurity content, which depend on the conditions of pyrolysis and the starting material.

Because of variation in these parameters many brands of carbon black are available for particular purposes.

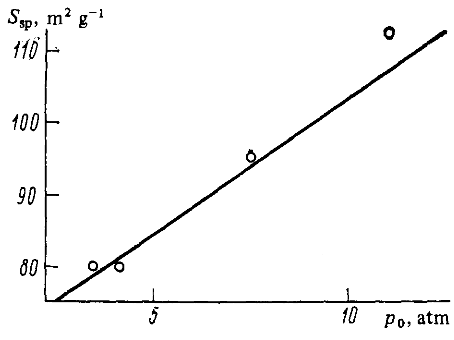

Figure 1. Dependence of specific surface of carbon black on initial pressure of acetylene[28].

In the above method the combustion itself does not lead to the formation of acetylene and carbon black, but has the ancillary role of providing a high temperature. Carbon black is produced not only by oxidative pyrolysis but also by other processes, e.g. the burning and detonation of acetylene (acetylene black)[27,28]. Fig. 1 illustrates the effect of the conditions on the characteristics of the product, showing the dependence of the specific surface of the carbon black on the initial pressure of acetylene[28].

A new method for the production of ethylene and acetylene is the so called immersion combustion of hydrocarbons[29,30]. Oxygen preheated to ~ 600°C is blown into a liquid hydrocarbon (e.g. kerosene), which vaporises and burns in the bubbles thus formed. After the oxygen has been used up, the hydrocarbon vapour is pyrolysed to ethylene and acetylene. Contact with the liquid phase results in effective quenching. The exhaust gases contain a substantial quantity of the required products.

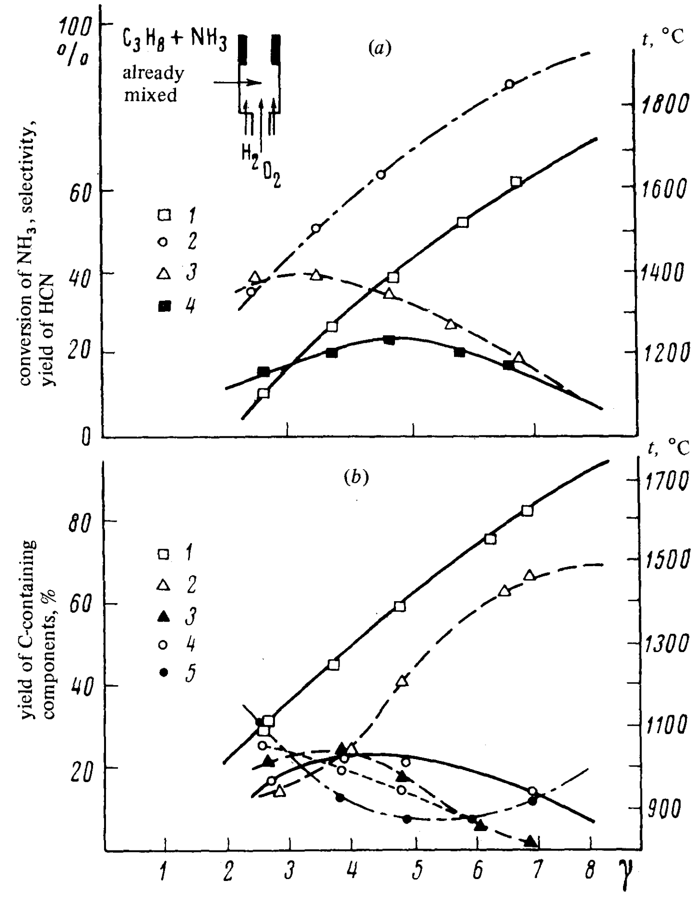

Figure 2. Dependence of combustion temperature and yield of carbon-containing products on ratio γ of space velocities of H_2–O_2 and C_3H_8–NH_3 mixtures[33]: (*a*) *1*) temperature; *2*) conversion; *3*) selectivity; *4*) yield of HCN (based on N); (*b*) *1*) temperature; and yields based on carbon of: *2*) CO; *3*) C_2H_4 + C_2H_2; *4*) CH_4; *5*) CO_2.

The combustion of hydrocarbons is used also for the production of hydrogen cyanide (manufacture of hydrocyanic acid). For this purpose ammonia is introduced either into the initial mixture or into the flow of combustion products[31-33]. The process can be represented empirically as

$$C_nH_{2n+2} + O_2 + NH_3 \to HCN + \ldots\ .$$

The yield of hydrogen cyanide (based on nitrogen) is high. The processes differ according to the raw material (e.g. with $n = 1$[31] or 3[33]) and the conditions of mixing of the reactants. The chief results obtained[33] for the synthesis of hydrogen cyanide are illustrated in Fig. 2.

2. Gas-flame Synthesis of Gaseous Products from the Elements

The reaction can be written

$$\underset{\substack{\text{fuel}\\ \text{element}}}{X_{L,G}} + \underset{\text{oxidant}}{Y_G} = \underset{\substack{\text{required}\\ \text{product}}}{Z_G}$$

where X and Y are the reactants and Z the reaction product. Combustion is easily conducted in burners or combustion chambers to a very high degree of completion: there are no fundamental difficulties in controlling the combustion. Further developments on these lines involve mainly intensification of the process and utilisation of the heat of combustion. In this respect a furnace technique, based on the solution of heat-engineering problems, has proved very effective[34].

The gas-flame synthesis of gaseous compounds from the elements has found widespread application in acid manufacture for the production of (*a*) hydrogen chloride (manufacture of hydrochloric acid)

$$H_2 + Cl_2 = 2HCl;$$

(*b*) sulphur trioxide (sulphuric acid)

$$S + O_2 = SO_2;$$

(*c*) phosphorus pentoxide (phosphoric acid)

$$2P + 2.5O_2 = P_2O_5.$$

3. Roasting of Sulphide Raw Material

This process[35–37] is interesting in giving simultaneously two required products having completely different purposes:

$$\underset{\text{fuel}}{MS_m} + \underset{\text{oxidant}}{\left(m + \frac{n}{2}\right)O_2} = \underset{\text{product I}}{MO_n} + \underset{\text{product II}}{m\,SO_2},$$

Metal oxides are used in metallurgy for the production of metals, and sulphur dioxide serves for the manufacture of sulphuric acid. Sulphide minerals are widely distributed in Nature (M = Fe, Mo, Cu, Ni, Zn, etc.).

Roasting is usually conducted in combustion reactors having a fluidised bed with an air blast. Particles of concentrate are continuously introduced, and the cinders (particles of oxide) are removed. Water is sometimes sprayed in to control the temperature. The variations in design of fluidised-bed vessels for the roasting of sulphide raw material have been discussed in detail[37]. The main difficulty is to achieve completeness of reaction. The process is characterised by comparatively low temperatures: for example, pyrites (FeS_2) is roasted at 800–900 and molybdenite at 600°C. Higher temperatures involve the formation of nodules, fusion, impaired access of air to the inner layers of particles, and lowered efficiency. It is interesting that the adiabatic temperatures for the combustion of sulphides are far higher than the roasting temperatures. For example, the combustion of molybdenum sulphide develops temperatures of ~ 1500°C in air, but above 3000°C in oxygen. Such a large difference between the maximum possible and the actual temperatures suggests that use of a fluidised bed is not the best method of organising combustion in roasting and that there are many opportunities for intensifying the process. Strictly speaking, the existing process of roasting bears little resemblance to combustion. Although it is close to homogeneous combustion, the considerable artifical lowering of temperature causes marked degeneration of the combustion. It is not by chance that the term "combustion" is not used in relation to this technique in the technical literature, and the combustion vessels are termed *furnaces*.

However, successful attempts have been made to organise the combustion of sulphides in a different manner. Thus the combustion of pyrites in a cyclone chamber with tangential feed gave a temperature of 1400°C, at which the oxide was molten, which made separation of the products more convenient[38]. The possibilities of using cyclone furnaces for the roasting of sulphides have been examined[39].

At the present time the two products are not manufactured together. In chemical industry the process is directed to the production of sulphur dioxide, while the metal oxides constitute low-quality by-products; the opposite situation occurs in metallurgy. This is also an indication of inadequate organisation of the process.

4. Blast-furnace Process

The blast-furnace process is one of the oldest and most important in metallurgy. It is based on the incomplete combustion of carbon, and can be represented schematically as

$$C + \begin{matrix} C + O_2 \rightarrow CO + Q; \\ \underset{\substack{\text{reducible}\\ \text{cpd.}}}{MO_m} \quad + Q \end{matrix} \rightarrow \underset{\text{product}}{M + \ldots .}$$

Carbon acts as both fuel and reducing agent. The burning of part of the carbon evolves heat, which raises the temperature of the mixture of the metal oxide with the rest of the carbon to values at which reduction to the metal takes place. At moderate temperatures carbon monoxide, formed by the combustion of carbon, also takes part in the reduction. The reduced metal is the desired product of the blast-furnace process.

The scheme of the process resembles oxidative pyrolysis: incomplete combustion also takes place here, and combustion has an ancillary role as a source of heat. However, the chemistry of the main reaction, leading to formation of the product, is essentially different.

The blast-furnace process is most widely used for the production of cast iron from iron ores:

$$\underset{\text{ore}}{\text{Iron}} + \underset{\substack{\text{fuel}\\ \text{(coke)}}}{\text{Carbon}} + \underset{\substack{\text{(limestone,}\\ \text{dolomite)}}}{\text{Fluxes}} + \text{Air} = \underset{\text{iron}}{\text{Cast}} + \text{Slags} + \underset{\text{gas}}{\text{Blast-furnace}}$$

A blast furnace (combustion chamber) consists of a hearth, in which the fuel burns and the charge melts, together with a shaft containing the melting material being fed to the hearth. The temperature in the hearth during the production of cast iron is 1300–1900°C.

Other metallurgical products, e.g. ferromanganese from manganese ores, are obtained by the blast-furnace method.

5. "Ex-furnace" Thermite Process

The main purpose of the thermite process[40–42] is to obtain metals from their oxides (or other compounds) by redox reactions in the condensed phase with the use of chemical elements as reductants. The chemical equation of the process is

$$\underset{\text{reducible cpd.}}{MX_m} + \underset{\text{reducing element}}{\frac{m}{n}M'} = \underset{\text{product}}{M} + \underset{\text{by-product (slag)}}{\frac{m}{n}M'X_n},$$

where M = Fe, Mn, V, Co, etc.; M′ = Ca, Al, Si, Mg, etc.; and X = O, Cl, etc.

Thermite processes have been known for a long time; the first experiments were made by Beketov during the nineteenth century.

If much heat is evolved in the thermite reduction, the process may take place under conditions of combustion. This case is referred to in metallurgical literature as an "ex-furnace"† thermite process. The example best known in the theory of combustion is the iron-aluminothermic process[43–45]

$$Fe_2O_3+2Al=2Fe+Al_2O_3.$$

An important practical task of the thermite process — the smelting of metals or alloys ‡ — can be achieved only if the metallic and slag phases in the combustion products separate out. For this it is necessary and sufficient that the temperature of combustion should be higher than the melting point of the products §, while the time of phase separation at the combustion temperature should be less than the thermal relaxation (cooling) time of the system.

The efficiency of extraction depends on the completeness of the redox reactions and the phase separation. Fig. 3 shows as example the dependence of the yield of metal on the particle sizes of iron oxide and of aluminium in the smelting of a ferroaluminium master alloy (80% Fe + 18% Al + 2% Si). The charge comprised 10 kg of iron oxide (98% Fe_2O_3) and 4.9 kg of aluminium powder (97% Al) with 0.8 kg of lime (90% CaO).[41] Study of ways for controlling thermite processes in order to ensure completeness in the main task of research in this field. One of the most effective methods is to introduce addivites for various purposes (slag-forming, preheating, etc.). The temperature of the thermite process is high, usually 2000–3000°C. The main charge and an ignition charge (primer) are placed in very simple open vessels with refractory walls and a hole for removal of the metal.

The thermite process has been most widely employed in ferrous metallurgy for the production of ferro-alloys and master alloys[41–46], most often with aluminium as reducing element.

Combined processes are also known, in which combustion is accomplished with an additional source of heat (preheating additives, raising the initial temperature of the charge by heating in a furnace). This extends considerably the range of systems in which combustion can be accomplished. The blast-furnace process can also be regarded as involving thermite reduction, with carbon as reducing element. However, the distinctive additional source of heat (the combustion of carbon in air) is responsible for a different, more complicated organisation of production.

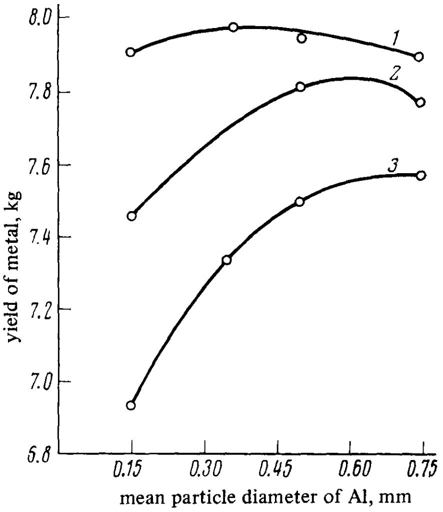

Figure 3. Effect of mean particle diameter of aluminium on yield of metal for different mean particle diameters of iron oxide (mm): *1*) 0.36; *2*) 0.55; *3*) 0.76.[41]

Thermite processes are used also to obtain non-ferrous metals[42]. However, the exploitation of combustion is less efficient than in the production of ferro-alloys and master alloys.

6. Self-propagating High-temperature Synthesis of Refractory Inorganic Compounds

This is the "youngest" technical combustion process[47–50]. Work in this field began in 1967, after discovery of the propagation of a combustion front in powdered mixtures of high-melting chemical elements, resulting in the formation of refractory compounds. Later other elements (of low melting point, liquid, and gaseous) were used for the synthesis. The general chemical scheme of the process, which has been termed *self-propagating high-temperature synthesis*, can be written.

$$\underset{\text{fuel elements}}{\sum_{i=1}^{m} a_i X_i} + \underset{\text{oxidising elements}}{\sum_{j=1}^{n} b_j Y_j} = \underset{\text{product}}{Z},$$

where X = Ti, Zr, Hf, V, Nb, Ta, Mo, W, etc.; Y = B, C, N, Si, S, Se, Al, etc.; and Z represents borides, carbides, nitrides, silicides, etc.

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† The term "ex-furnace" is unfortunate, firstly, because it is terminologically inexact. The word "ex-furnace" implies that a furnace exists but that the process is for some reason conducted outside it, somewhere at its side. The sense would have been conveyed more accurately by "non-furnace" or "furnaceless". Secondly—perhaps the most important—the term indicates not the essential nature of the process but a technical consequence (absence of a furnace). In this sense it is more correct to speak of self-propagating thermite processes.

‡ Alloys are obtained by reducing two (or more) compounds together.

§ Very often the combustion temperature is higher also than the melting points of the reactants, and the reduction accompanying combustion occurs entirely in the liquid phase.

The elements X are in the form of powdered metals, the Y elements are used in powdered, liquid, or gaseous states, and the product Z is refractory and usually solid at the combustion temperature. The first group of elements (metals) act as fuels, and the latter group (non-metals) as oxidising agents. Chemical reaction between the elements takes place in the condensed phase, even if one of the reactants is a gas. In most of the processes the reaction is accompanied by the evolution of a large quantity of heat, which is responsible for the possibility of combustion. Thus this process involves a strongly exothermic reaction between chemical elements in a condensed phase taking place under combustion conditions.

The usual forms of the process with $m = 1$ and $n = 1$ have now been supplemented by other variants ($m \neq 1$ and $n \neq 1$), leading to the production of more complicated compounds:

(*a*) $m = 1$, $n = 2$ (carbonitrides MC_xN_y, where M = Ti, Zr, Nb, Ta);[51]

(*b*) $m = 2$, $n = 1$ ($Nb_xZr_{1-x}N$,[51] $Mo_xNb_{1-x}S_2$, $Ti_xCr_{1-x}B_2$, $Ti_xW_{1-x}C$);[52,53]

(*c*) $m = 2$, $n = 2$ (mixed carbonitride $Nb_xZr_{1-x}C_yN_z$).[51]

This process entails some of the highest combustion temperatures (~2500–4000°C).

Three types of processes can occur depending on the state of aggregation of the elements— (1) combustion of mixtures of X and Y powders in a vacuum of an inert gas (e.g. production of carbides, borides, and silicides), (2) combustion of powdered X in the gaseous oxidant Y (e.g. production of nitrides by burning metals in gaseous nitrogen), and (3) combustion of powdered X in a liquid oxidant Y (e.g. production of nitrides by burning metals in liquid nitrogen). The powders may first have been compressed or may be used in a loose state.

Special reaction vessels are used, different for each of the above three modifications of the process. The most common at present are gas-free synthesis vessels for processes of type (1).[54] A characteristic feature of the self-propagating high-temperature processes is the absence of by-products. Together with the possibility of complete conversion of the reactants (theoretical yields), this enables high-quality refractory products to be obtained, satisfying the most rigorous modern requirements with respect to materials behaviour.

An example is the production of titanium carbide, which is effectively used in the compositions of solid alloys, high-temperature materials, and abrasive pastes. Investigation of the mechanism of the combustion of mixtures of powdered titanium and carbon blacks[55] has helped to establish the main factors controlling the rate and the completeness of synthesis, among them the particle size of the titanium, the density of the pellets and the proportions of reactants in the charge, and the removal of heat from the combustion products. The experimental linear burning velocity varied[55] over the range 0.5–5 cm s^{-1} depending on the parameters of the initial mixture. The calculated adiabatic temperature was 3200 K, and the experimental temperature ~ 3000 K.[56]

Research on the mechanism of combustion of the titanium–carbon sytem has led to the development of the efficient technical production of titanium carbide[53] by a batch process in vessels of capacity 4–10 litres. This technology permitted the experimental production of high-quality titanium carbide powders. The product obtained from PTS (or PTM) titanium powder and Pm-15TS carbon black under optimum conditions contained (% by weight) 19.6–19.8 combined carbon, 0.1 uncombined carbon, 0.1 oxygen, and traces of nitrogen.

Various combined processes are now being developed, one of them involving the self-propagating high-temperature synthesis and thermite processes. A possible scheme is

$$\underset{\substack{\text{reducible}\\\text{product}}}{MX_m} + \underset{\substack{\text{element}\\\text{(reductant}\\\text{and oxidant)}}}{Y} \rightarrow \underset{\text{product}}{MY_n} + \underset{\text{by-product}}{YX_k},$$

An example is the reaction[57]

$$WO_3 + 3B = WB + B_2O_3.$$

The essence of this combined process is that the metal—one of the reactants in the self-propagating process—is formed by a prior thermite reaction. The combined process is cheaper than the self-propagating process alone, but gives products of poorer quality.

The self-propagating high-temperature method has at present found its widest application for the production of powdered refractory compounds, although other applications may be of interest (the manufacture of solid articles, the deposition of coatings, and the synthesis of single crystals). The general scheme of utilisation of these processes and products is shown diagrammatically in Fig. 4.

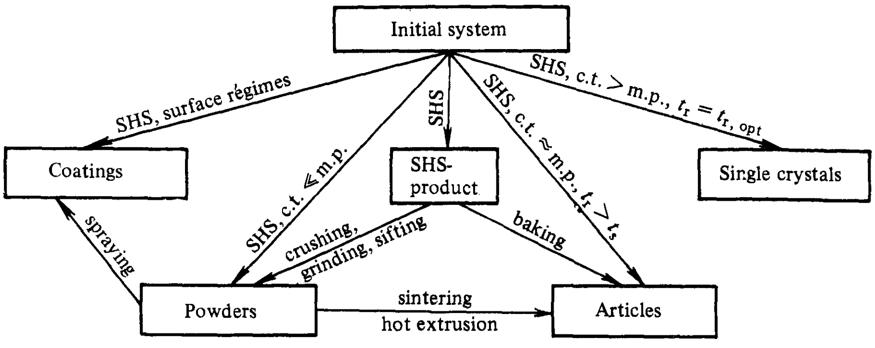

Figure 4. Diagram of uses of self-propagating high-temperature synthesis (SHS) processes and products: c.t. = combustion temperature; m.p. = melting point of product; t_r = thermal relaxation (cooling) time of product; $t_{r,\,opt}$ = optimum value of t_r; and t_s = duration of sintering.

Principal indices of technical combustion processes.

Process	Raw material	Product	State of aggregation of product under normal conditions	Principal applications	Combustion		State of aggregation of reactants in combustion zone	Chemical nature of combustion
					régime	temp., °C		
Combustion of C_xH_y	natural gas	unsat. C_xH_y, process gas, carbon black	gas, solid	organic synthesis	layer, homogeneous	1300–1700	gas	oxidation, pyrolysis
Gas-flame synthesis	S, P	oxides	gas	acid production	layer, homogeneous	1000–2500	gas	synthesis from elements
Oxidising roast	sulphides	oxides	gas, solid	acid production, metallurgy	homogeneous	600–900	gas, solid	oxidation
Blast-furnace process	iron ore	cast iron	solid	metallurgy	homogeneous	1600–1900	solid, liquid	redox
Thermite	oxide, Al	ferro-alloys, master alloys	solid	metallurgy	layer	2000–3000	liquid	redox
SHS	powdered metals and non-metals	refractory compounds	solid	inorganic materials	layer	2500–4000	gas, liquid solid	synthesis from elements

The most common technical combustion processes have been outlined above. They differ in many characteristics—the raw material used, the state of aggregation and purpose of the products, the chemistry of the reaction, the conditions and temperature of combustion, etc. Their main unifying feature is that the products of combustion contain a useful substance, which provides the reason for carrying out the process. The Table compares the main features of the processes that have been described.

III. COMBUSTION AS A TECHNICAL CHEMICAL PROCEDURE

1. Technical Features of Combustion

We shall now examine the chief specific features of combustion that permit its use in chemical technology, drawing where possible a comparison with the most widely used furnace and rapidly developing plasma processes. Almost all the peculiarities of combustion are due to its strongly exothermic character. This is responsible for the high temperatures of burning and the absence of external supplies of energy. The high temperatures in turn produce high reaction velocities and complete conversion of starting materials into end-products ¶.

When the reaction goes to completion, condensed products are of high quality and gaseous products are obtained in high yields †. The extremely high reaction velocities lead to high outputs. Since an external supply of energy is unnecessary, the equipment is simple and reliable. These factors are responsible for the favourable economics of the process. In chemical technology combustion is thus a highly efficient method for obtaining high-quality products cheaply.

Combustion is intermediate between furnace and plasma processes with respect to physical parameters (temperature ‡ and rate), but surpasses them considerably in certain technical parameters, primarily the consumption of electrical energy and the equipment. An almost negligible quantity of energy is required to initiate combustion, and the process itself takes place entirely on the basis of the intrinsic energetic possibilities of the system. Furnace and especially plasma processes require an immense consumption of electrical energy to produce the high temperatures involved. Simple equipment — combustion vessels, burners — is used for combustion, it is reliable in operation, with an almost unlimited life. High-temperature furnaces and especially plasmatrons are less reliable, with a short life, since the heating elements often deteriorate because of the high energy intensity. Thus the development of plasmachemistry is held back at the present time largely by the absence of improved plasmatrons.

¶ At high temperatures the reversibility of combustion may become evident (e.g. in dissociation of the product), with consequent thermodynamic incompleteness of conversion. On cooling, however, the thermodynamic equilibrium of the combustion products is usually displaced towards formation of the required product, and by controlling (if necessary diminishing) the rate of cooling we can eliminate the incompleteness of reaction due to thermodynamic factors. The equilibrium can be influenced also by varying the pressure and the temperature of combustion.

† When the required product is an intermediate the situation is more complicated.

‡ For various systems the temperature of combustion usually lies in the range 1000–4000° C; the temperature of furnace processes does not exceed 2500°C, and the mass-average temperature of the jet in plasmachemical processes reaches 10 000°C.

Combustion has wide possibilities when technical processes are conducted in large plant units. The fundamental difficulties associated with the change in scale from laboratory apparatus to industrial plant do not usually exist for combustion processes: very often combustion takes place more easily and more completely in large than in small volumes.

The possibility of accomplishing combustion at high and ultrahigh pressures is of great importance. In many cases fundamentally new constructions are not required, and modern high-pressure apparatus can be used. The combination of high pressures with high temperatures in furnace processes involves great difficulties, and high-pressure plasmatrons do not exist at all.

The erroneous opinion is held among technologists that technical processes based on combustion are difficult to control. An understanding of the factors governing the rate and the completeness of the chemical reactions involved will enable effective methods of control to be established. Particular combustion régimes can be deliberately maintained by regulating the temperature by the introduction of an additional source of energy or dilution of the initial reactants with the products, by varying the pressure and the concentrations in the reaction zone, by establishing a definite disperse composition when condensed phases are involved, and by other methods.

From a survey of the above considerations it may be concluded that combustion is one of the most ideal processes of chemical technology. It is therefore desirable to obtain products where possible under conditions of combustion.

2. Conditions for the Accomplishment of Processes of Chemical Technology under a Combustion Régime

In considering the possibility of conducting technical processes under combustion conditions we must pose two questions: (i) when can combustion be accomplished at all; and (ii) when can combustion be used for technical purposes.

The first question is answered by combustion theory[12]. The precise quantitative solution depends on many factors—the kinetic character of the combustion (simple or stepwise reactions, slight or marked kinetic inhibition by reaction products), the state of aggregation of the reactants, the combustion régime (homogeneous or layered steady state or oscillatory), etc. Fundamentally, however, the solution is common to all cases. We shall therefore examine for simplicity the propagation of a combustion wave during a first-order reaction in the gas phase.

In theory there exist necessary and sufficient conditions for a combustion wave to be propagated. The necessary conditions are

$$\beta = \frac{R(CT_0 + Q)}{CE} \ll 1;$$

$$\gamma = \frac{R(CT_0 + Q)^2}{CEQ} \ll 1,$$

where Q is the heat of reaction, E the activation energy, C the heat capacity at constant pressure § (molar or specific depending on the units in which Q has been expressed), T_0 the initial temperature of the reactants, and R the gas constant. These conditions evidently include the reaction parameters of combustion Q, E, and C, together with T_0 characterising the initial state of the system.

The sufficient condition is determined from the relation between the evolution of heat in the combustion wave and the loss of heat to the surrounding medium. In order that a combustion wave shall be propagated, it is sufficient that the heat losses should be less than a critical value: $\eta < \eta_{cr}$. The quantity η can be determined from the formula

$$\eta = \frac{T_{adb} - T_c}{T_{adb} - T_0},$$

where T_c is the temperature of combustion in the presence of heat losses. For the present example

$$T_{adb} - \frac{RT_{adb}^2}{E} \leqslant T_c \leqslant T_{adb}$$

so that

$$\eta_{cr} = \gamma.$$

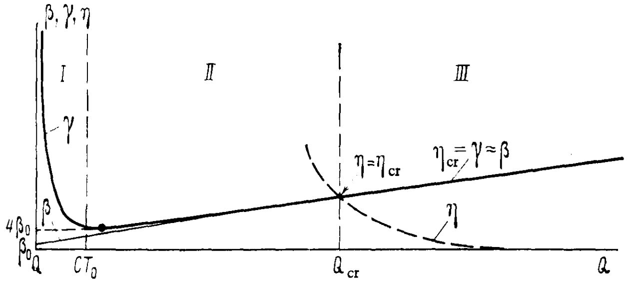

Figure 5. Necessary and sufficient conditions for propagation of combustion waves.

For clarity the necessary and sufficient conditions can be shown graphically. Fig. 5 illustrates the dependence of β, γ, and η on Q for constant T_0 and E with $\beta_0 = RT_0/E \ll 1$ ¶. The heat of reaction is chosen as variable on this graph, since it is the most important characteristic of the combustion. In most cases, when the composition of the products is known or can readily be assumed, the heat of reaction can be determined from thermochemical considerations. Three characteristic ranges (I)–(III) can be distinguished in Fig. 5, characterised by small, medium, and large heats of reaction.

(I) A combustion wave cannot be propagated, since the necessary conditions cannot be observed because of the large value of γ. Rates of reaction at T_{adb} and T_0 are comparable, and the pattern of propagation of a reaction zone through the substance, which is characteristic of combustion, is impossible.

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§ In the theory of combustion we use the mean heat capacity determined by means of the formula

$$C = \frac{1}{T_{adb} - T_0} \int_{T_0}^{T_{adb}} C_p(T)\,dT,$$

where T_{adb} is the adiabatic (thermodynamically calculable) temperature of combustion.

¶ Strictly speaking, such a relation with a constant activation energy can be obtained only by diluting the initial reactants with inert products, but qualitatively it represents a more general rule. Special effects, not considered in the theory, arise when the heat of reaction is very large.

(II) The necessary conditions are observed, but the sufficient condition is not satisfied. A combustion wave cannot be propagated, since heat losses from the reaction zone are large. If combustion is initiated by special means, it is unable to develop, and dies out.

(III) Both necessary and sufficient conditions are observed, and the process has all the characteristic features of combustion. Usually $Q \gg CT_0$ and $\beta \simeq \gamma$.

A similar situation occurs in other, more complicated cases. There is no definite boundary between ranges (I) and (II). The critical heat of reaction Q_{cr}, separating ranges (II) and (III), is quite specific, and is determined in the theory of combustion limits[12] from the critical condition for propagation of a combustion wave. It depends both on the kinetic factors characterising the rate of evolution of heat in the combustion wave and on the geometric and thermophysical factors characterising the conditions of combustion. The latter include the geometrical scale of the burning system (the diameter of the specimen, tube, or jet) and the effective heat-transfer coefficient from the reaction zone to the surrounding medium. Even under the same conditions the critical heat of reaction may vary greatly on passing from one system to another. Whether or not a given system will burn cannot be predicted merely on the basis of information on the heat of reaction. The various classifications of the ability of exothermic systems to burn, based on values of this parameter and detached from the kinetic characteristics of the system and the thermophysical circumstances, are therefore untenable. Furthermore, determination of the critical conditions of combustion in any specific case is unreal—despite the theoretical possibilities—both because methods of calculation have been inadequately developed and because the data necessary for the calculation are lacking.

In such a situation a preliminary analysis can most reasonably be made by calculating thermodynamically the adiabatic temperature of combustion. Although the result will not give an unambiguous answer to the question, it is always useful, since some experience of working with a given class of systems enables a correct appraisal to be made of the possibility of combustion in a particular system. For example, experimental studies of the self-propagating high-temperature synthesis of four classes of refractory compounds—carbides, borides, nitrides and silicides — show that combustion does not occur when $T_{adb} < 1500$ K, systems always burn when $T_{adb} > 2500$ K, and additional investigations are required for intermediate values.

The answer to the second question — when combustion can be used for technical purposes—depends on the technical demands made. Here the main indicators are the yield and the possibility of isolating the product, its quality (for condensed substances), and the cost of the starting material. Detailed discussion of these criteria is innecessary, so that we shall merely examine a few examples.

It has already been noted that metal and slag phases should separate in the thermite production of ferro-alloys and master alloys. If such separation does not take place, the combustion cannot be used for the preparation, because of the difficulty of isolating the product. Phase separation is clearly possible when the combustion temperature is higher than the melting points of all the combustion products. For it to be complete, however, the operating conditions must ensure long thermal relaxation times, so that the system does not cool before complete phase separation can occur. The theory of the thermite process[41] has established criteria indicating the possibility of metal extraction in any specific case, and has suggested methods for controlling the process (preheating or slag-forming additives, the combination of combustion and furnace methods, etc.).

Complete conversion is very important to self-propagating high-temperature processes, in order to avoid contamination of the product with unchanged reactants, as isolation (i.e. purification) of the product is almost impossible. For the same reason single-phase products should be obtained.

The production of acetylene and ethylene by incomplete combustion of a hydrocarbon is possible only if adequate quantities of intermediate products of the pyrolysis of hydrocarbons are formed and if effective quenching is ensured.

It must be remarked, however, that the conditions of technical combustion depend on how the process is organised, and with correct organisation are very often feasible. It is therefore more important to satisfy conditions under which combustion can in general be accomplished (in systems whose use is economically justified).

IV. SOME PROMISING LINES OF ADVANCE IN THE USE OF COMBUSTION PROCESSES IN CHEMISTRY AND TECHNOLOGY

Analysis of the possibilities for applying combustion to chemical production suggests that only a small proportion of useful processes have yet been exploited. For this reason the development of research on combustion towards technical objectives offers great promise.

Firstly, we may note that the application of combustion processes to the chemistry and technology of inorganic materials is a novel and little investigated problem. Great prospects are opened up, whose full scope is at present difficult to envisage. The variety of factors characterising the composition and structure of powdered inorganic compounds and materials based on them leads to difficulties in establishing the scientific foundations of control for ensuring that quite definite products are obtained. The use of combustion methods for these purposes presents a difficult and fascinating scientific problem, whose solution is closely connected with the need to develop the theory of combustion.

Among promising tasks is firstly expansion of the range of inorganic compounds formed by interaction of the elements under conditions of combustion (it is the easiest). Here we may have in mind the synthesis of semiconducting compounds (sulphides, selenides, tellurides, phosphides, etc.), refractory compounds based on rare-earth metals, refractory one-phase composite compounds (mainly multicomponent solid solutions), and new modifications of binary compounds under conditions of combustion at high and ultrahigh pressures, etc.

It is of interest to apply self-propagating high-temperature processes to compounds of metals (e.g. chlorides and oxides), firstly because the use of a cheaper material than powdered metals will lower the cost of refractory compounds and secondly because the volatile components (chlorides) will permit combustion in the gas phase yielding the products as with homogeneous gas-phase deposition) in the form of powders of high specific surface, which is important for certain applications. It is tempting to try to transfer gas-phase precipitation to combustion conditions (by analogy with the transfer of certain furnace processes in the self-propagating high-temperature method). However, systems with chlorides or oxides as components are in most cases insufficiently exothermic, so that the main problem is to compound (select) high exothermic combinations. Here a thermodynamic approach may prove very effective. A thermodynamic analysis of the combustion of several systems involving chlorides has been made[58]. As an example[40], the reaction

$$BCl_3 + NH_3 = BN + 3HCl$$

is weakly exothermic and leads to an adiabatic temperature rise of only 500–600 deg. Nevertheless, the introduction of a gaseous mixture of hydrogen and chlorine into the initial mixture may raise the adiabatic temperature considerably and make possible the establishment of a combustion régime. The consequent decrease in the yield of the nitride from the boron is not very great. Analogous methods can be used in other cases.

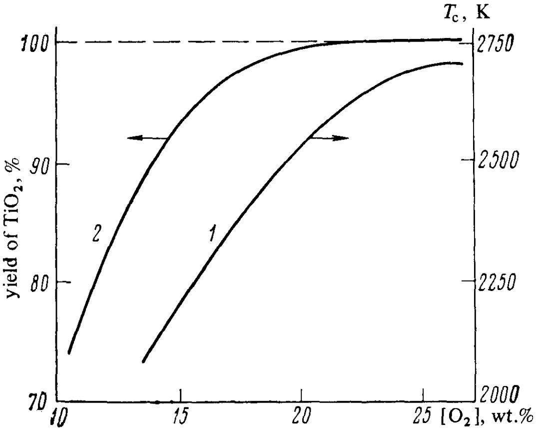

Figure 6. Thermodynamic calculation for $TiCl_4 + O_2 + H_2$ system with H : Cl $\simeq$ 2 and p = 1 atm: *1*) combustion temperature; *2*) yield of TiO_2.

An important practical task is to obtain titanium dioxide pigment from the tetrachloride:

$$TiCl_4 + O_2 = TiO_2 + 2Cl_2 \ .$$

This reaction is at present accomplished in the jet of an oxygen plasma, which is one of the greatest achievements of plasmachemistry[59]. It is therefore especially interesting to examine the possibilities of combustion for solving this problem. The temperature of adiabatic reaction between titanium tetrachloride and oxygen is ~ 1200 K,[60] which may be too low for combustion. However, the introduction of hydrogen into the initial mixture (giving titanium dioxide together with hydrogen chloride) will establish quite good thermodynamic conditions for combustion to occur (Fig. 6). The main difficulty in the experimental investigation will evidently be to control the degree of dispersion and the phase constitution of the dioxide with the aim of satisfying technical requirements.

Zel'dovich has put forward the interesting idea that cyanogen and its decomposition products might be used as reductants. Mixtures of cyanogen and oxygen develop very high temperatures on combustion, so that the excess of cyanogen could efficiently be used for gas-phase reduction (and probably for nitriding).

An important practical problem is to make solid articles from refractory compounds or composite materials by combustion. Its solution will lead to the introduction of combustion methods into powder metallurgy, which will undoubtedly aid progress. At present combustion methods yield refractory compounds in the form of powders, from which articles are produced by the usual sintering processes of powder metallurgy. However, sintering often takes place during combustion. It would be useful to study the completeness of sintering as a function of the combustion conditions and to learn how to control the process. Articles may then be obtained directly from the initial components under a combustion régime in a single technical stage. Compositions occupy a special position in the problem, and attempts have been reported[61] to obtain solid mixtures by combustion.

Several other types of use of combustion processes in the chemistry and technology of inorganic materials are of interest — the employment of surface combustion for the application of coatings for various purposes, the growing of single crystals by cooling liquid or condensing gaseous combustion products, etc.

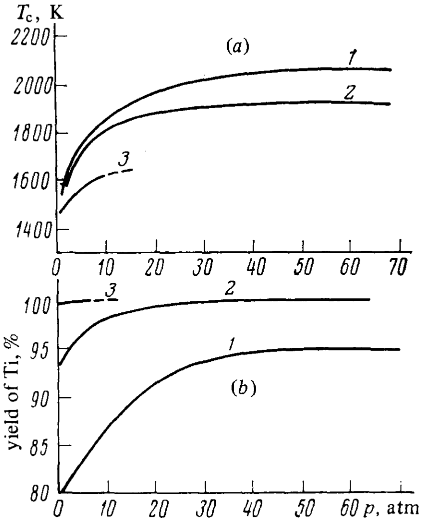

Figure 7. Pressure dependence of: *a*) combustion temperature; *b*) yield of titanium for $TiCl_4$ + Mg system containing different proportions (%) of magnesium: *1*) 20 (stoichiometric); *2*) 22; *3*) 24.

There are also several important but little developed uses of combustion in metallurgy and chemical technology. The production of non-ferrous metal powders, e.g. titanium, offers great possibilities. One of the most familiar methods for obtaining titanium is based on the thermite reaction[62]

$$TiCl_4 + 2Mg = Ti + 2MgCl_2.$$

In industry it is accomplished by molten magnesium with a spray of titanium tetrachloride by a furnance method (to give so called titanium sponge). However, this reaction is sufficiently exothermic to be of interest from the viewpoint of combustion. The results of special thermodynamic calculations[58] illustrated in Fig. 7, together with some preliminary experiments, show that magnesium is able to reduce the tetrachloride to titanium under a combustion régime, and this process should be of industrial importance. The main task is evidently to examine the quality of the titanium obtained in this way. It can readily be shown that several other metals may be produced by analogous processes. An interesting problem is to obtain metal powders of different degrees of dispersion, as well as powdered alloys.

The oxidation of sulphides offers great opportunities for the application of combustion methods. As already remarked, existing processes for roasting sulphide ores in a fluidised bed are inefficient, since the energy reserves of the system itself are by no means fully utilised (the working temperatures in the technical process are far lower than the combustion temperatures actually obtainable). It appears useful to examine the possibilities of combustion in a stream of a highly dispersed sulphide and oxygen (or air greatly enriched with oxygen). Very high temperatures will develop, and lead to a qualitatively different mechanism of oxidation. It can be regarded[39] as involving two stages, in the first of which sulphur burns to form its oxides. Combustion takes place in the vapour phase. The thermal flux from the combustion front heats a particle to a high temperature and causes thermal dissociation of the sulphide. Thus the first stage involves the burning of sulphur vapour, and the metal plays no part in the reaction. This mechanism recalls the burning of a hydrocarbon drop as described by Varshavskii[63]. In the second stage the residue, consisting of the metal (or a lower sulphide) burns away, by either vapour-phase or heterogeneous combustion depending on the relation between the combustion temperature and boiling point of the metal (see theory of combustion of metal particles[64]). By this mechanism oxidation processes should go to completion.

The use of combustion methods to obtain chemical reagents shows promise. The self-propagating high-temperature method, for example, is able to yield chemically pure specimens of many inorganic compounds. Borovinskaya et al.[65] have recently produced salts of certain inorganic acids by combustion processes:

$$NH_3 + H_2 + Cl_2 \rightarrow NH_4Cl;$$

$$V_2O_5 + Mg \rightarrow MgVO_4:$$

$$CaO + C + O_2 \rightarrow CaCO_3.$$

Simple and mixed gases have been obtained[66] by the combustion of pyrotechnic compositions, which may be of practical value under specific conditions.

The above is a by no means complete list of promising lines of research on combustion processes in chemical technology.

V. TECHNICAL PROCESSES AND COMBUSTION THEORY

We shall now consider the relation between problems of chemical technology and combustion theory. We have already noted in the Introduction the extremely small contribution made by chemical technology to the general theory of combustion, whose development was stimulated mainly by energetic problems. Indeed, the development of such processes as the blast-furnace production of cast iron, the roasting of sulphide ores, and the manufacture of acetylene did not present to the science of combustion a single major problem of general theoretical importance.

An exception is the work by Tesner and his colleagues[24] on the formation of soot in flames, in connection with the problem of obtaining carbon black. The importance of this work extends beyond the specific problem, since the burning of gases accompanied by the formation of condensed products is very widespread and is met in various applied processes. An understanding of the mechanism of formation of a condensed phase in the circumstances will permit not only control of the state of dispersion of condensed combustion products (which is of direct practical importance) but also development of the theory of the combustion of gases to take into account the influence of the kinetics and the thermodynamics of condensation processes on the rate of burning (establishment of a theory of so called "condensation" combustion).

However, it would be erroneous to assume that known technical combustion processes do not contain interesting theoretical problems: such problems exist, and are by no means few. We shall discuss some of them.

The immersion preparation of acetylene and ethylene involves the combustion of a gas bubble. This type of combustion of heterogeneous systems (in contrast to that of drops of fuel suspended in a gaseous oxidant) remains almost uninvestigated. The limited volume of oxidant, the intense heat transfer from the combustion zone to the liquid phase, the continuously increasing volume of the hot hearth, the stepwise chemical reaction, and other features may be responsible for several interesting effects of theoretical importance.

It is no less important to extend the theory[67] of the stepwise combustion of gases to exothermic oxidation accompanied by endothermic pyrolysis as in the incomplete combustion of hydrocarbons. Such a theory should reveal the factors primarily responsible for the structure of the combustion zone, in order to indicate ways of establishing high concentrations of intermediate products and of obtaining them in high yield by the optimum application of quenching media (when an intermediate is the required product) or of ensuring completeness of combustion (when a final product is required). Attempts have been made to give a detailed mathematical description of the process taking into account all possible reactions. However, it would be more useful to formalise the description[67] and consider only the most important stages.

The above account indicates that the problem of stepwise combustion arises also in the roasting of sulphides. Here, however, it extends to the diffusion combustion of heterogeneous systems. The stepwise burning of particles and their aggregates is an almost undeveloped branch of combustion theory.

Interesting theoretical problems of combustion are connected also with the thermite extraction of ferro-alloys and master alloys. One of these is to develop a theory of liquid-phase gas-free combustion allowing for diffusion processes. Interest in this arises from the use under industrial conditions of coarse granules of reactants and the fact that the limiting kinetic régimes of theory are not realised in liquid-phase combustion. A diffusion-kinetic theory of liquid-phase processes of gas-free combustion should indicate ways of diminishing the incompleteness of thermite reactions caused by diffusion hindrances. Another problem[46] is the possibility of explosion in the combustion of highly exothermic compositions (such as molybdenum trioxide with aluminium) in large quantities owing to gas formation resulting from partial vaporisation of the reactants.

The development of self-propagating high-temperature processes was from the very beginning closely connected with combustion theory. The peculiar forms of conversion of the reactants has led to the development of new trends in combustion theory, and the large range of new substances to the discovery of hitherto unknown phenomena. The mechanism of gas-free[20,55,68-71] and filtration[72-74] combustion has been investigated, the phenomena of spin[75,76] and oscillatory[20,68,75-77] combustion have been observed, régimes of surface and layer-by-layer combustion[72-74], the propagation of a combustion front, and burning down[55,70-72] have been studied, and methods have been worked out for calculating the rate of propagation of a combustion wave with broad zones of chemical reaction[71,78].

Although the survey in this section is incomplete, it indicates that not only energetics but also technology has given rise to many interesting problems in combustion theory.

* * *

Combustion can occupy an important position in modern chemistry, with its tendency to intensify processes and accomplish new reactions by establishing so called "extreme" conditions. The purpose of this Review was to direct attention to this. Highly intensive technical chemical processes have already been organised on the basis of combustion, and there are clear prospects for the further development of this trend. Problems in chemical technology may be expected to give a new impetus to the development of combustion theory.

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The Development of Methods for the Description of Adsorption Isotherms within the Framework of the Fundamental Postulates of Langmuir's Theory

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The review deals with the problem of the form of isotherms for adsorption on homogeneous and inhomogeneous surfaces with and without dissociation when the adsorbate molecule occupies a single elementary site on the surface or several such sites, for polymolecular adsorption, and for adsorption in the micropores.
The bibliography includes 74 references.

CONTENTS

I. INTRODUCTION OF FUNDAMENTAL POSTULATES

The equilibrium in adsorption can be characterised by specifying the adsorption isotherm:

$$v = \mathrm{f}(p), \tag{1}$$

where v is the amount of adsorbed gas (or vapour) and p the equilibrium pressure, and the form of the function

$$Q = \mathrm{f}_1(v), \tag{2}$$

where Q is the differential heat of adsorption.

Depending on the characteristics of the surface, the nature of the adsorbent, temperature, and pressure, the functions expressed by Eqns.(1) and (2) may be varied.

In the present review, adsorption is considered mainly within the framework of the adsorption theory the foundations of which were laid by Langmuir. However, initially we shall consider briefly the pre-Langmuir concepts concerning the nature of the phenomena at the interface between the solid and the gas or vapour. The first theoretical ideas about the adsorption of gases and vapours were put forward by Arrhenius in 1911 [1] and were somewhat later treated mathematically by Eucken[2]. Arrhenius began with the van der Waals hypothesis that there is no sharp phase transition between the liquid and its vapour and that there is a transitional layer the properties of which vary continuously from those of the liquid to those of the vapour on moving away from the surface of the liquid. Since the adsorbability sequence for various gases and vapours agrees with the condensability sequence, Arrhenius assumed that the adsorption forces are of the same type as molecular forces and hence are functionally related to the force constant in the van der Waals equation.

Developing this view, Eucken believed the transitional layer to be a miniature atmosphere whose molecules are retained near the surface under the influence of a potential ϵ, which is a function of the distance between the adsorbed molecule and the surface[2]:

$$\varepsilon = c/\mathrm{f}(r)\ , \tag{3}$$

where c is a constant which depends on the nature of the adsorbent and the adsorbate. In contrast to Eucken, Bakker [3] assumed that the molecules in the transitional layer attract one another with a force that decreases exponentially with increase of the distance between them.

Polanyi went further than other investigators in his development of Arrhenius's ideas, his first studies on this problem having been published in 1916.[4] He believed that the force field near the adsorbent should have the same properties as the gravitational field, i.e. it cannot be shielded, does not influence the interaction of the adsorbed molecules, and is independent of temperature, but, in contrast to the gravitational field, is specific. The degree of adsorption was calculated from the distribution of the potential, i.e. it was necessary to know the form of the relation $\epsilon = f(\varphi)$, which defines the volume of the space over the adsorbent surface in which the potential is greater then ϵ. In Polanyi's theory, this relation defines an infinite family of isotherms and permits the calculation of the degree of adsorption at any specified temperature. The nature of the $f(\varphi)$ curve, expressing the distribution of the potential, was determined from a single adsorption isotherm recorded below the critical temperature of the adsorbate. The required distribution was obtained as a result of the simultaneous solution of the equations

$$\varepsilon = RT\ln(p_0/p) \tag{4}$$

and

$$\varphi = v/d, \tag{5}$$

where p_0 is the vapour pressure at a temperature T and d the density of the adsorbed substance in the liquid state at the temperature T. Polanyi assumed that the forces of cohesion between the molecules are due to the fact that the latter are polarised in a specific manner.

Later London showed[5] that, when two particles are sufficiently close to one another, their electrons move in such a way that the states in which the electrons of both species are displaced in the same direction relative to their nuclei are statistically preferable. This phenomenon is a result of the interaction of the instantaneous dipole moments, and is responsible for the presence of the cohesion forces.

The postulates constituting the basis of Polanyi's theory have been frequently criticised (see, for example, McBain[6]), and, although numerous experimental data are consistent with this theory, towards the beginning of the 1930's it was already widely believed that not only the adsorption of gases but also the adsorption of vapours (in the initial stage) must be described in terms of Langmuir's ideas and not those of Polanyi (see, for example, Dubinin[7]). On this basis of the physical concepts of Polanyi's theory, Zhukhovitskii[8] formulated in 1938 a theory of adsorption from real solutions and compared its conclusions with experimental data. Quantitative tests showed that the formulae of the potential theory conflict with experiment; for example, in order to explain the position of the adsorption maximum as a function of the concentration of carbon tetrachloride in benzene, it was necessary to assume an average adsorption potential of 85 000 cal, which is quite unrealistic for van der Waals forces. The predictions of the theory were not fulfilled even qualitatively. Thus the component for which the theory predicted negative adsorption underwent position adsorption from solutions which were dilute with respect to it. Zhukhovitskii's results[8] throw doubt on the physical picture of adsorption constituting the basis of Polanyi's theory.

The foundations of the modern adsorption theory were laid in 1916 by Langmuir[9], who assumed that, on each unit area of the crystal surface, there should be a definite number of sites capable of adsorbing gaseous molecules. More molecules can be adsorbed only as a result of the formation of additional molecular layers. The forces acting between two layers of adsorbed gas molecules must be much smaller than those acting between the surface layer of the crystal and the first layer of adsorbed molecules. The rate of evaporation from the second layer is usually much higher than from the first layer, so that the number of molecules in the second layer must be negligibly small. When a gas molecule collides with a section of the surface already coated by a layer of adsorbed molecules, it usually re-evaporates so rapidly that the phenomenon is indistinguishable from reflection. According to Langmuir, in the adsorption of vapours at pressures approaching the saturation vapour pressure there should be a tendency for the thickness of the adsorbed films to become greater than one monolayer.

Langmuir began with the postulate that the forces acting between the atoms of the crystal and those of the adsorbed substance are of the same type as the forces acting between the adjacent atoms of the crystal; the manifestation of these forces is a result of the chemical unsaturation of the surface atoms in the crystal. (A similar idea had been expressed somewhat earlier by Haber[10].) The residence time of the adsorbed molecules on the surface depends on the strength of the surface forces.

Langmuir considered quantitatively the following six cases of adsorption.

(1) The surface consists of elementary areas of the same kind (henceforth we shall refer to such a surface as homogeneous) and the gas is adsorbed in the form of molecules each of which occupies a single elementary site.

(2) The surface consists of more than one kind of elementary site and adsorption takes place as in case 1.

(3) Adsorption on an amorphous surface (henceforth such surfaces will be referred to as inhomogeneous).

(4) Adsorption on a homogeneous surface, but on each elementary site more than one adsorbed molecule may be retained.

(5) Adsorption with dissociation on a homogeneous surface.

(6) Deformation of adsorbed films on a homogeneous surface having a thickness greater than the value corresponding to one molecule.

The process leading to the formation of adsorbed films with a thickness greater than the value corresponding to one molecule is referred to as polymolecular adsorption, in contrast to monomolecular adsorption (cases 1–5), in which the thickness of the adsorbed layer does not exceed the value corresponding to one molecule.

The Langmuir isotherms are considered below and the progress in adsorption theory for the cases enumerated above is analysed. To facilitate the exposition, the different cases of adsorption have been grouped in a manner different from that used in Langmuir's study[11].

II. ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE IN THE ABSENCE OF INTERACTION BETWEEN THE ADSORBED MOLECULES

1. Each Adsorbate Molecule Occupies One Elementary Site on the Adsorbent Surface

In 1916[9] and then in 1918[11] Langmuir published a kinetic derivation of the equation of the isotherm for this simplest case. Suppose that θ_0 is the fraction of the free adsorbent surface, i.e. the ratio L/N, where N is a number of adsorbed molecules per cm^2 of the surface under the conditions of maximum adsorption (i.e. in this case the number of elementary sites per cm^2) and L the number of adsorbed molecules per cm^2 of the surface, θ_1 the fraction of the occupied surface ($\theta_1 = 1 - \theta_0$), and Z_0 the number of collisions of the adsorbate molecules with 1 cm^2 of the adsorbent surface per second, and, according to the kinetic theory of gases, we have

$$Z_0 = \frac{N_0 p}{\sqrt{2\pi MRT}} \tag{6}$$

(N_0 is the Avogadro number and M the molecule weight of the gas); if the pressure is expressed in mmHg, then

$$Z_0 = 3.52 \times 10^{22}\, p/\sqrt{MT}. \tag{7}$$

Suppose that α is the probability of adhesion, i.e. the ratio of the number of molecules adsorbing to the number of molecules colliding with the surface per unit time (on a completely free surface) and β is the rate of desorption of the adsorbed molecules from the fully coated surface.

We then have at equilibrium

$$(1-\theta_1)\,\alpha Z_0 = \beta\theta_1, \tag{8}$$

whence

$$\theta_1 = \alpha Z_0/(\beta + \alpha Z_0). \tag{9}$$

If $\alpha/\beta = \sigma_1$, the Eqn.(9) transforms into

$$\theta_1 = \sigma_1 Z_0/(1 + \sigma_1 Z_0). \tag{10}$$

This is the required adsorption isotherm. Introducing the notation $ap = \sigma_1 Z_0$, where a is a constant, we have

$$\theta_1 = ap/(1 + ap). \tag{11}$$

Eqn. (11) can be formulated in the form of the equation of a rectangular hyperbola:

$$\theta_1 = a\left(\frac{1}{p} + a\right)^{-1}. \qquad (12)$$

For this reason, Eqn. (11) is sometimes referred to as the hyperbolic adsorption isotherm. For values of p so small that $ap \ll 1$, we have

$$\theta_1 = ap, \qquad (13)$$

i.e. Henry's equation holds. If p is so large that $ap \gg 1$, then

$$\theta_1 \rightarrow 1. \qquad (14)$$

Under these conditions, Eqn. (11) can be written in the form

$$ap(1-\theta_1) = 1, \qquad (15)$$

i.e.

$$1-\theta_1 = \theta_0 = 1/ap. \qquad (16)$$

Thus, when the degree of surface coverage tends to unity, the fraction of the free surface is inversely proportional to the pressure.

The problem of whether or not experimental data are described by isotherm (11) is usually elucidated with the aid of one of the following methods.

One can use the equation

$$\frac{p}{\theta_1} = \frac{1}{a} + p, \qquad (17)$$

obtained by rearranging Eqn. (11). Eqn. (17) describes a linear plot of p/θ_1 against p and makes it possible to determine a from experimental data.

The second method involves the use of the equation of a linear plot of p/v against p:

$$\frac{p}{v} = \frac{p_{1/2}}{v_\infty} + \frac{p}{v_\infty} \qquad (18)$$

where v_∞ is the maximum degree of adsorption corresponding to the formation of a monolayer and $p_{1/2}$ the pressure at which $v = \frac{1}{2}v_\infty$. Eqn. (18) can be obtained from the expression

$$v = v_\infty p/(p_{1/2} + p), \qquad (19)$$

which in its turn can be obtained from Eqn. (11) if account is taken of the fact that $\theta_1 = v/v_\infty$ and $1/a = p_{1/2}$ [the latter is a consequence of Eqn. (11)]. This method makes it possible to determine $p_{1/2}$ and hence also a and v_∞, provided that Eqn. (18) holds.

The following procedure is sometimes used to compare experimental data with isotherm (11).[12] After some rearrangement, logarithms are taken in Eqn. (8), which yields

$$\ln(\theta_1/p) = \ln a + \ln(1-\theta_1). \qquad (20)$$

For not unduly high values of θ, we have

$$\ln(1-\theta_1) \simeq -\theta_1, \qquad (21)$$

since the series expansion

$$\ln(1-\theta_1) = -\left[\theta_1 + \frac{1}{2}\theta_1^2 + \frac{1}{3}\theta_1^3 + \ldots\right] \qquad (22)$$

is valid. For this reason Eqn. (20) can be replaced approximately by the equation

$$\ln(\theta_1/p) = \ln a - \theta_1, \qquad (23)$$

which describes a linear plot of $\ln(\theta_1/p)$ against θ_1. If isotherm (11) describes the experimental data, the slope of the straight line should be -1; the value of a can then be determined from the intercept on the ordinate axis.

Temkin[13] obtained Eqn. (11) by a statistical method. He used for this purpose the partition function for the adsorbed layer (Z_a):

$$Z_a = (f_a)^N \cdot \frac{L!}{N!\,(L-N)!}\ , \qquad (24)$$

where f_a is the partition function of the molecule adsorbed in a specific manner, N the number of molecules in the adsorbed layer, L the number of surface sites, and $(f_a)^N$ the partition function of the adsorbed layer in which the molecules can be accommodated in only one way. Substitution of Z_a in the expression for the Helmholtz free energy and differentiation with respect to L yield the equation of the chemical potential of the adsorbed state. After setting the chemical potential of the adsorbed state equal to the chemical potential of the gas, i.e. assuming equilibrium, Temkin obtained Eqn. (11). This shows that Eqn. (11) is valid for the given case of adsorption regardless of the mechanism by which adsorption equilibrium is attained. Temkin established a relation between the constant a in Eqn. (11) and the heat of adsorption†. We shall restrict the treatment by quoting only the approximate equation, analogous to the approximate Nernst formula[16] for interphase equilibria, since the exact equation contains the heat capacity of the adsorbed layer, which is as yet unknown for the vast majority of adsorbent–adsorbate systems. The approximate equation is

$$\lg\frac{1}{a} = -\frac{Q}{4.57T} + 1.75\lg T + i', \qquad (25)$$

where i' is the so called conventional chemical constant, which can be assumed to be approximately equal to 3 for molecules and 1.5 for atoms, and Q is the heat of adsorption.

2. The Adsorption Isotherm for Polyatomic Molecules Dissociating on the Surface into Mobile Atoms (Mobile Films)

Suppose that the adsorption of each atom requires a single elementary site. The necessary condition for the adsorption of a diatomic molecule colliding with the surface is then the presence of two adjacent free elementary sites. The probability that any of the elementary sites on the surface is free equals $1-\theta_1$. When the adsorbed atoms can migrate on the surface (mobile films), the probability that any two adjacent sites on the surface are free is equal to the product of the probabilities that each is free, i.e. equals $(1-\theta_1)^2$. The necessary condition for the desorption of diatomic molecules from the surface is the presence of adsorbed atoms on two adjacent elementary sites on the surface. The probability of such an event is θ_1^2. Then the condition for the equality of the rates of adsorption and desorption at equilibrium is

$$\alpha(1-\theta_1)^2 Z_0 = \beta\theta_1^2. \qquad (26)$$

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† In non-Soviet literature, priority in the statistical derivation of isotherm (11) is frequently given to Fowler (see, for example, Trapnell[14]), who published his study two years later than Temkin[13].

This equation was obtained by Langmuir[11]. After substitutions, we obtain

$$ap(1-\theta_1)^2=\theta_1^2. \tag{27}$$

The positive solution of Eqn. (27) is

$$\theta_1=\sqrt{ap}/(1+\sqrt{ap}). \tag{28}$$

For low coverage, when $\theta_1 \ll 1$, Eqn. (28) becomes

$$\theta_1=\sqrt{ap}, \tag{29}$$

i.e. the degree of adsorption is proportional to the square root of the pressure. For an almost completely covered surface, where $(1-\theta_1) \ll 1$, we have

$$(1-\theta_1)=\sqrt{1/ap}. \tag{30}$$

If the molecule dissociates on the surface into three species, each of which occupies a single elementary site, then, when $\theta_1 \ll 1$, we have

$$\theta_1=\sqrt[3]{ap}, \tag{31}$$

and, when $(1-\theta_1) \ll 1$, we have

$$(1-\theta_1)=\sqrt[3]{1/ap}. \tag{32}$$

In order to test whether or not the experimental data are described by Eqn. (28), it is convenient to put the latter in the form

$$\frac{\sqrt{p}}{v}=\frac{1}{\sqrt{a}\cdot v_\infty}+\frac{\sqrt{p}}{v_\infty}. \tag{33}$$

Eqn. (33) describes a linear plot of $\sqrt{p}/v$ against $\sqrt{p}$, its slope yielding the volume of the monolayer v_∞ and the intercept on the ordinate axis yielding the value of a.

A second method for comparing the experimental data with Eqn. (28), which is applicable at pressures such that $\sqrt{ap} \ll 1$, is as follows. One can use the equation

$$\ln(\theta_1/\sqrt{p})=\ln\sqrt{a}-\sqrt{a}\sqrt{p}, \tag{34}$$

which is obtained by rearranging Eqn. (28) and taking logarithms, provided that one subsequently replaces $\ln(1+\sqrt{ap})$ by the first term of the series expansion

$$\ln(1+\sqrt{ap})=\sqrt{ap}-\frac{1}{2}ap+\frac{1}{3}ap\sqrt{ap}-\frac{1}{4}a^2p^2+\ldots \tag{35}$$

Eqn. (34) describes the straight line

$$\ln(\theta_1/\sqrt{p})-\sqrt{p}.$$

Temkin[13] derived Eqn. (28) by a thermodynamic method and showed that, in order to describe the relation between the coefficient a and the heat of adsorption, one can employ the approximate Eqn. (25).

3. The Adsorption Isotherm of a Gas Each Molecule of which Occupies More than one Elementary Site on the Surface (Mobile Films)

If the molecules are adsorbed without dissociation, then the activation energy for their migration on the surface must be lower than the activation energy for desorption, since migration does not require the complete dissociation of the bonds between the adsorbed molecules and the adsorbent. Therefore, when the gas adsorbed without dissociation is desorbed at an appreciable rate at any temperature, the adsorbed film cannot be stationary.

The exact adsorption isotherm for this case is unknown in a general form, although various workers undertook the solution of this problem, which is frequently encountered in practice. An approximate solution in the most general form has been given by Ostrovskii and Temkin[17,18]. The calculation is performed by a kinetic method, i.e. by equating the expressions for the rates of adsorption and desorption. The resulting equation is solved for p (or θ_1). The equation for the rate of adsorption will be formulated as follows:

$$r_+=\alpha p\, f(\theta_1), \tag{36}$$

where $f(\theta_1)$ is a function of the degree of surface coverage, which has to be determined. We shall consider, as an example, the adsorption of molecules (for example those of benzene) such that each requires seven elementary sites ($n = 7$) distributed on the surface as shown in the Figure; each adsorbent atom has six nearest neighbours; $z = 18$ is the number of surface sites which can be occupied on rotation of the adsorbed molecule about the fixed site which it occupies (0), which is not included in the number z; such a surface corresponds to the (111) face of a cubic crystal. We shall consider on the adsorbent surface a group of atoms (each of which is the centre of an elementary site), consisting of the central atom 0 and its 18 neighbours 1, 2, 3, ..., 18 (see Figure). If the central atom is occupied, the implication is that one of the septets of atoms 0, 6, 7, 8, 9, 2, 1 or 0, 1, 9, 10, 11, 3, 2 or 0, 2, 11, 12, 13, 4, 3, etc. is occupied, while the other sites can be occupied or free. If the central atom is free, then any of the atoms 1–18 can be either occupied or free. One must take into account the fact that the adsorption of each molecule reduces the probability of adsorption on the neighbouring sites; for example, the centre of the molecule adsorbed next to that shown in the Figure can no longer be located at points, 5, 4, 3, etc.

$f(\theta_1)$ was calculated in terms of Bethe's approximation[19]. It was assumed that the probability of any given distribution can be formulated thus:

$$g\xi^{An_0+Bn_1}\xi_1^{n_0}\xi_2^{n_1}, \tag{37}$$

where ξ_1 is the probability that the central atom is occupied, ξ_2 the probability that any one of the 18 atoms closest to the central atom is occupied, $n_0 = 0$ if the central atom is free, $n_0 = 1$ if the central atom is occupied, n_1 is the number of occupied atoms nearest to the central atom (with the exception of those contained in the same septet as the central atom if the latter is occupied), ξ is introduced to take into account the fact that ξ_1 and ξ_2 are not independent, A and B are constants, and g is the statistical weight of the given distribution.

The relative probability of any given distribution is

$$g\varepsilon_1^{n_0}\varepsilon_2^{n_1}, \tag{38}$$

where

$$\varepsilon_1=\xi^A\xi_1 \text{ and } \varepsilon_2=\xi^B\xi_2. \tag{39}$$

The values of g corresponding to various combinations of n_0 and n_1 were calculated[17]. Next the average number of species at the sites closest to the central site were determined for cases where the central atom is occupied and free and $\epsilon_2 = f(\theta_1)$ was calculated. The probability expressed in terms of ϵ_2, that there are on the surface seven free sites distributed in such a way that the given molecule can be adsorbed on them, was determined. Having expressed ϵ_2 in terms of θ_1, the required equation of the rate of adsorption was obtained. For the adsorption of a molecule resembling that of benzene on the (111) face of a cubic crystal, one obtains

$$r_+=\alpha'\ \alpha_0'\ p(1-\theta_1)^7\left(\frac{3}{3-\theta_1}\right)^6. \tag{40}$$

Apart from Eqn.(40), Ostrovskii and Temkin[17] also derived the corresponding equations for the adsorption of a molecule on four sites, as shown in Figs.*b* ($n = 4$, $z = 8$) and *c* ($n = 4$, $z = 6$). Generalisation by induction of the three equations obtained leads to the expression

$$r_+ = \alpha'(n, z)\,\alpha_0'\,p(1-\theta_1)^n\left[\frac{z}{z-(n-1)\theta_1}\right]^{n-1}. \tag{41}$$

For $n = 2$ [when $n = 2$, $\alpha'(n,z) = 1$ and $\alpha = \alpha_0'$], Eqn.(41) yields

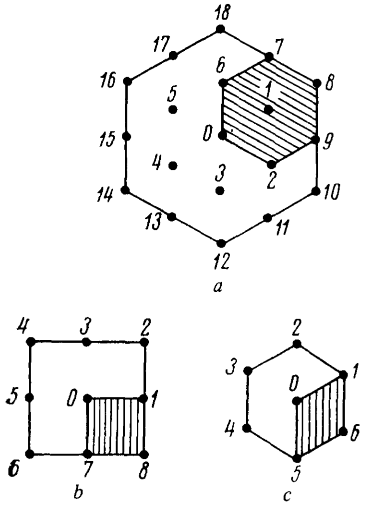
$$r_+ = \alpha_0'\,p(1-\theta_1)^2\frac{z}{z-\theta_1}, \tag{42}$$

which agrees with the equation obtained earlier by Roberts and Miller using the same approximation[20]. Ostrovskii and Temkin[17] quote numerical values of $\alpha'(n,z)$ for certain typical combinations of n and z. In the case under consideration, the equation for the rate of desorption (r_-) is

$$r = \beta\theta_1. \tag{43}$$

Eqns.(41) and (43) lead to an adsorption isotherm of the following type[18,21]:

$$p = \frac{1}{a}\cdot\frac{\theta_1}{(1-\theta_1)^n}\cdot\left[1-\frac{1}{z}(n-1)\theta_1\right]^{n-1}. \tag{44}$$



A model of adsorption on the (111) face of a face-centred cubic crystal (*a* and *c*) and on the (100) face of a cubic crystal (*b*).

When $n = 1$, Eqn.(44) leads to Eqn.(11). When $n = 2$ and $z = 2$, i.e. for the adsorption of a molecule on two sites in the case of a linear arrangement of sites, Eqn.(44) yields

$$p = \frac{1}{a}\frac{\theta_1}{(1-\theta_1)^2}\cdot\frac{2-\theta_1}{2}. \tag{45}$$

As a result of an exact solution by the thermodynamic method, Temkin[22] obtained the adsorption isotherm for molecules resembling carbon monoxide on two centres for a linear arrangement of sites:

$$p = \frac{1}{a}\frac{\theta_1(2-\theta_1)}{2(1-\theta_1)^2}. \tag{46}$$

In comparing isotherms (46) and (45), one must bear in mind that, for molecules such as carbon monoxide, the factor 2 appears in the partition function owing to the asymmetry of the molecule. In the adsorption of symmetrical molecules, for which Eqn.(44) was derived, this factor should not appear. This implies that isotherms (45) and (46) agree numerically. Thus Bethe's approximation leads to the exact result for the one dimensional case.

If $1/a$ is defined as the proportionality coefficient between p and θ_1 in the range where $\theta_1 \ll 1$, isotherm (44) predicts a more rapid increase of p with θ_1 then isotherm (11). For example, in the case considered above with $n = 7$, $z = 18$, and $\theta_1 = 0.5$, we obtain, according to Eqn.(11), $p = 1/a$ and, according to Eqn.(43), $p = 10.7/a$. In order to show whether or not the experimental data for the relation between p and θ_1 are described by Eqn.(44), one determines $1/a$, as described above, from data obtained in the region where $\theta_1 \ll 1$. Theoretical $\theta_1 - p$ curves calculated by Eqn.(44) are then plotted for the postulated value of n and for values of z corresponding to the presence of four or six nearest neighbours at each surface adsorbent atom (the most frequently encountered cases for crystalline materials). The points corresponding to the experimental results are then drawn on the same plot and their positions are compared with the positions of the theoretical curves.

III. ADSORPTION ISOTHERMS ON INHOMOGENEOUS SURFACES IN THE ABSENCE OF INTERACTION BETWEEN THE ADSORBED MOLECULES

The problem of the form of adsorption isotherms on inhomogeneous surfaces was formulated for the first time by Langmuir[11], who called such surfaces "amorphous", assuming that, as a rule, on the surfaces of [crystalline] solids there are elementary sites of only one or a few different types, while on amorphous materials such as glass all the areas can have different adsorption capacities. In such cases the surface may be regarded as divided into infinitesimally small regions $d\rho$, each of which is characterised by a specific value of a. If the law governing the distribution of sites with respect to adsorption capacity is known, i.e. if the form of the function $a(\rho)$ is known, the overall adsorption can be obtained by integration with respect to all the values of ρ:

$$\frac{L}{N} = \int_0^1 \frac{pa(\rho)\,d\rho}{1+pa(\rho)}. \tag{47}$$

Later Taylor[23,24] developed the idea that the surface of crystalline materials must be inhomogeneous with respect to catalytic activity and adsorption capacity. According to Taylor, the atoms located on the surface of the crystal faces are the most "saturated" (the saturation of valence forces is considered); the atoms located on the crystal edges are less saturated and those at the crystal vertices are saturated to a still smaller extent. If this is the case, there may be differences also between the atoms located on different crystal faces, near lattice defects, etc. As a result, the activation energy for adsorption and the rates of adsorption and desorption will differ at different surface sites.

1. The Adsorption Isotherm on a Surface Characterised by a Linear Distribution of Elementary Sites with Respect to Adsorption Capacity

The adsorption isotherm for this case was obtained by Temkin[25]. Following Temkin, we shall assume that the different areas on the surface are characterised by different adsorption capacities, i.e. different values of a in Eqn.(11). The interaction forces between the adsorbed species will be neglected, so that the relative distribution of the adsorbed molecules may be disregarded. We shall imagine that all the elementary areas on the surface are numbered in order of decreasing values of a (1, 2, 3, ..., N, ..., L). We shall denote by s the fraction of the surface traversed on moving along it from area to area in the direction of increasing ordinal number of the latter, i.e. the relative number of the site (N/L). According to the earlier hypothesis concerning the multiplicity of the values of a, the latter is a monotonic function of s. At the same time, in order to examine the dependence of a on s, Temkin considered the variation of the heat of adsorption (per molecule) ϵ with s on the basis that a and ϵ are linked by the equation

$$a=\frac{F_a}{F_g kT}\cdot e^{\varepsilon/kT}, \tag{48}$$

where F_a and F_g are the partition functions of the adsorbate molecule in the adsorbed and gaseous states. Suppose that the relation between ϵ and s is given by the equation

$$\varepsilon=\varepsilon^0-cs, \tag{49}$$

where c is a constant and $\epsilon^0=\epsilon$ when $s=0$. According to Eqn.(48),

$$a=a_0e^{-f_1s}, \tag{50}$$

where $a_0=a$ for $s=0$ and

$$f_1=c/kT. \tag{51}$$

Following Temkin, we shall refer to surfaces for which Eqn.(49) is satisfied as linearly inhomogeneous surfaces.

For adsorption without dissociation, we have

$$\theta_1=\int_0^1\frac{ap\,\mathrm{d}s}{1+ap}. \tag{52}$$

After substituting Eqn.(50) in (52), we obtain

$$\theta_1=\int_0^1\frac{a_0e^{-f_1s}p\,\mathrm{d}s}{1+a_0e^{-f_1s}p}, \tag{53}$$

and after integration we have

$$\theta_1=\frac{1}{f_1}\ln\frac{1+a_0p}{1+a_1p}, \tag{54}$$

where $a_1=a_0e^{-f_1}$, i.e. $a_1=a$ when $s=1$, so that

$$f_1=\ln(a_0/a_1). \tag{55}$$

If the surface is strongly inhomogeneous, i.e. if $a_0\gg a_1$, it is possible to distinguish a range of pressures in which the following inequalities hold:

$$a_0o\gg 1,\quad a_1p\ll 1, \tag{56}$$

i.e. the most strongly adsorbing areas are almost all occupied, while the least strongly adsorbing areas are almost all free. Temkin refers to this region as the region of moderate surface coverages. If inequality (56) holds, then we have the approximate relation

$$\theta_1=\frac{1}{f_1}\ln a_0p. \tag{57}$$

In the literature, Eqn.(57) is usually referred to as the Temkin isotherm. An isotherm of this type was put forward for the first time by Frumkin and Shlygin[26] as an empirical formula for the description of the behaviour of the platinum electrode in acid solutions in the region of the so called hydrogen arrest.

At low surface coverages, where $a_0p\ll 1$, the Temkin isotherm transforms into the equation

$$\theta_1=(a_0-a_1)\,p/f_1, \tag{58}$$

if following the series expansion

$$\ln(1+x)=x-x^2/2-x^3/3-\ldots \tag{59}$$

only the first term is retained. Eqn.(58) is analogous to Henry's law. If $a_0\gg a_1$, then

$$\theta_1=a_0o/f_1. \tag{60}$$

This equation leads to an interesting conclusion. The heat of adsorption calculated from the proportionality coefficient between the adsorption and pressure in the Henry region on a uniformly inhomogeneous surface should differ by only RT from the heat of adsorption on the most active sites (since f_1 is inversely proportional to T). This conclusion may be of interest, particularly for gas chromatography, where the method for the determination of the heats of adsorption from Henry's constant is widely used.

For the adsorption of diatomic molecules with dissociation into atoms on a uniformly inhomogeneous surface, the isotherm is

$$\theta_1=\frac{1}{f_1}\ln\left(\frac{1+\sqrt{a_0p}}{1+\sqrt{a_1p}}\right)^2, \tag{61}$$

which gives rise at moderate coverages to the following approximate equation equivalent to Eqn.(57):

$$\theta_1=\frac{1}{f_1}\ln a_0o, \tag{62}$$

At low coverages, Eqn.(61) leads to the expression

$$\theta_1=\frac{2}{f_1}\sqrt{a_0o} \tag{63}$$

[cf. Eqn.(29) for a homogeneous surface]. In order to test whether or not the experimental data at moderate coverages are described by Eqn.(57) or (62), it is sufficient to demonstrate the linearity of the plot of θ_1 against $\ln p$. The slope of the resulting straight line is equal to the ratio kT/c and a_0 can be determined from the intercept on the ordinate axis.

2. The Adsorption Isotherm on a Surface Characterised by Exponential Inhomogeneity

Exponentially inhomogeneous surfaces are those with an exponential distribution of the elementary areas with respect to adsorption capacity. We shall define the distribution function in the form

$$\mathrm{d}L=CL\,e^{-\frac{\varepsilon-\varepsilon_1}{k\Theta}}\mathrm{d}\varepsilon, \tag{64}$$

where ϵ_1 is the minimum heat of adsorption on the least strongly adsorbing sites, Θ a constant having the dimensions of temperature, and the constant C can be found from the normalisation condition

$$\int \mathrm{d}L = L, \tag{65}$$

which yields

$$C = \gamma/kT, \tag{66}$$

where

$$\gamma = T/\Theta. \tag{67}$$

The equation of the adsorption isotherm will be formulated as follows:

$$\frac{L}{N} = \int_{\varepsilon_1}^{\varepsilon_0} C\mathrm{e}^{-\frac{\varepsilon-\varepsilon_1}{k\Theta}} \frac{a_1 p \exp[(\varepsilon-\varepsilon_1)/kT]}{1 + pa_1 \exp[(\varepsilon-\varepsilon_1)/kT]} \mathrm{d}\varepsilon. \tag{68}$$

The problem of the form of the isotherm for the case under consideration was examined for the first time by Zel'dovich[27], who showed that, in the range of moderate coverages [which corresponds to the integration of Eqn.(68) in the range from $\epsilon_0 = \infty$ to $\epsilon_1 = 0$], an isotherm of the following form is obtained:

$$\theta_1 = \frac{\pi\gamma a_1^\gamma}{\sin \pi\gamma} \cdot p^\gamma. \tag{69}$$

Temkin and Levich[28], who, unlike Zel'dovich, carried out the integration with respect to surface coverages and not energies, later obtained the same equation for the region of moderate coverages. The constant γ is proportional to T and $0 < \gamma < 1$. When it is assumed that $\Theta = \infty$ (i.e. $\gamma = 0$) in Eqn.(64), then at moderate coverages, i.e. with $(1/a_0) \ll p \ll (1/a_1)$, Eqn.(69) leads approximately to the logarithmic Temkin isotherm [Eqn.(62)]. If $\gamma = 1$, then the following equation holds approximately at moderate coverages[28]:

$$\theta_1 = a_1 p \ln(1/a_1 p). \tag{70}$$

A general solution of Eqn.(68), from which it is possible to obtain Eqn.(69) as a special case, was published recently[29].

An equation of type (69) is usually referred to as the Freundlich isotherm. Freundlich[30] was the first to use the expression

$$v = cp^{1/n} \tag{71}$$

for the description of numerous data on adsorption equilibria over a wide range of pressures and temperatures. If the Freundlich isotherm is valid, then at moderate surface coverages the plot of θ_1 against $\lg p$ is a straight line whose slope is equal to γ.

Apart from the derivation of the equation for monomolecular adsorption on the basis of a specified law governing the distribution of sites with respect to adsorption capacity, Temkin and Levich[28] solved in a general form the converse problem of the determination of the type of distribution of sites with respect to their adsorption capacity when the form of the adsorption isotherm is known. The solution was applied to the logarithmic isotherm, the Freundlich isotherm, and certain other isotherms. In particular, it was shown by this method that the Schmidt–Il'in isotherm[31,32] cannot be obtained for any distribution of sites on an inhomogeneous surface with respect to adsorption capacity. In other words, this isotherm cannot be represented as the limiting sum of isotherms (11).

IV. ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE WITH INTERACTION BETWEEN THE ADSORBED SPECIES

The decrease of the heat of adsorption with increasing surface coverage of the adsorbent can be caused either by the inhomogeneity of the surface or by the operation of repulsion forces between the adsorbed species. Repulsion forces consist of the repulsion forces between the filled electron shells of the adsorbed species, which diminish rapidly with distance, and the forces which decrease comparatively slowly with distance. The latter can be of different types. The possibility of effects associated with the mutual influence of the adsorbed species was pointed out for the first time by Langmuir[33]. Somewhat later the results of measurements of the heats of adsorption of hydrogen on tungsten were explained[34] with the aid of the hypothesis of repulsion forces.

Langmuir[33] assumed that the interaction forces between the adsorbed molecules in a two-dimensional monolayer film are the same type as the forces responsible for the deviation of the equation of state for real gases from the equation for an ideal gas. In the derivation of the equation of state for the adsorbed layer, the virial equation for a two-dimensional gas is used:

$$FS_0 = RT - \frac{1}{2}\Sigma rf, \tag{72}$$

where F is the two dimensional pressure, S_0 the surface area containing 1 gram-atom of the adsorbate, and f the interaction force, which is a function of the distance r; the summation is carried out with respect to all the pairs of adsorbed atoms on the surface. Langmuir obtained the equation of the adsorption isotherm in the form

$$\theta_1 = \frac{\alpha p\, \mathrm{e}^{m/T}}{A_{1.5} T^{3/2}}, \tag{73}$$

where $A_{1.5} = 7.98 \times 10^6$ atm $K^{-3/2}$ is a constant and m is a constant related to the heat of adsorption Q by the equation $Q = n(m + lT)$, where n and l are constants and $m = f(\theta_1)$. Later the problem of the role of the interaction of the adsorbed species due to the operation of dipolar forces was examined by Temkin[25], who obtained an equation for the isotherm representing in an explicit form the relation between the pressure and the degree of coverage. Like Langmuir, Temkin began with the virial theorem for a two-dimensional gas, but, unlike Langmuir, restricted the treatment to surface coverages for which it is possible to neglect the cases of the simultaneous interaction of three and more gas molecules. The interaction law was used in the following form:

$$\varepsilon(r) = \mu^2/r^3, \tag{74}$$

where μ is the dipole moment of the adsorbed molecule. Temkin derived the equation of the adsorption isotherm from the equation of state for the adsorbed layer with the aid of the Gibbs equation:

$$L = \frac{1}{kT} \frac{\partial F}{\partial \ln p}. \tag{75}$$

This leads to the Williams isotherm, proposed[35] as the empirical formula

$$\ln(p/L) = BL + C, \tag{76}$$

where B and C are constants. If the interaction forces are fairly large, then, as shown by Temkin[25], Eqn.(76) differs little from that of the logarithmic isotherm for not unduly low values of L (in the region of moderate coverages). Under these conditions, Eqn. (76) is close to

$$\theta_1 = \frac{1}{A} \ln a_0 p. \tag{77}$$

The constant a_0 has the same significance as a_0 in the logarithmic isotherm [Eqn. (57)]. We have $A = BN$, where

$$B = 2\pi \int_0^\infty (1 - e^{-\varepsilon(r)/kT})\, r\, d\, r.$$

Thus the physical significance of the constant A differs from that of the constant f_1 in Eqn. (57) and is characterised by a different temperature dependence.

The authors [25,33] assume that the interaction is determined by forces of the same type as that in molecules of real gases. The physical picture underlying these equations can explain only a decrease of the heat of adsorption per mole of gas of the order of RT. In practice an appreciably greater reduction of the heat of adsorption is frequently observed as the surface becomes saturated.

Kobozev and Gol'dfel'd [36] examined the interactions associated with the effect involving the fixation of the adsorbed atoms on the surface. They assumed that, in the adsorption at any centre, there is a change in the adsorption potential not only of the given centre, in consequence of the saturation of the adsorption forces, but also a decrease of the adsorption potential extending over a number of neighbouring adsorption centres (since the atoms of the solid are close-packed). On moving away from the occupied centre, the attenuation of the adsorption potential decreases in accordance with a law of the type

$$\varphi_r = \varphi_0 - \varphi_0 \cdot f(r) = \varphi_0 [1 - f(r)], \tag{78}$$

where φ_r is the potential of the adsorption centre at a distance r from the occupied centre with $[\partial f(r)/\partial r] < 0$. A characteristic feature of this approach is the assumption that the repulsion of the molecules in the adsorbed layer is due to the polarisation of the adsorbent itself and not to the interaction of the adsorbent molecules. According to the authors, interactions of this type can extend over extremely long distances, are intense, and should occur for both polarised and electrically symmetrical adsorbed species. The adsorption isotherm is derived using the equation of state of a two-dimensional gas in the form

$$\left(F - \frac{\Delta}{A_2^2}\right)(A_2 - A_1) = RT, \tag{79}$$

where A_2 is the area of the entire surface, A_1 twice the area of the adsorbed molecules themselves, and $\Delta = f_1[\varphi_0, f(r)]$. The equation of the adsorption isotherm is

$$p/\theta_1 = p + C \cdot \exp[\varphi_0(1 - \psi(\theta))/RT]\ ‡, \tag{80}$$

where $\varphi_0[1 - \psi(\theta)]$ is the adsorption energy and C a constant.

A graphical method for the calculation of the values of $C \exp\{\varphi_0[1 - \psi(\theta)]/RT\}$ from the experimental $p/\theta - p$ adsorption isotherms has been described [36]. It makes it possible to compare the theory with experimental results.

Vol'kenshtein [37] examined the problem of the form of the adsorption isotherm for different laws governing the interaction between the adsorbed species. He assumed that the interaction is independent of the relative orientation of the molecules and that the interaction forces are not capable of being saturated. The equations for the rates of adsorption (r_+) and desorption (r_-) are

$$r_+ = Z_0 a (1 - \theta_1) \cdot \exp[-E(\theta_1)/RT], \tag{81}$$

$$r_- = \beta\theta_1 \exp[-(\Delta Q(\theta_1) + E(\theta_1))/RT], \tag{82}$$

where E is the activation energy for adsorption.

Under conditions of equilibrium, Eqns. (81) and (82) lead to the expression

$$\Delta Q(\theta_1) + RT \ln[(1 - \theta_1)/\theta_1] = RT \ln(1/\sigma_1 p). \tag{83}$$

Assuming that the adsorbed atoms on the surface are located at the sites of a square lattice, Vol'kenshtein found that

$$\theta_1 = (r_0/r)^2 \tag{84}$$

(r_0 is the minimum possible distance between two adsorbed molecules and r the shortest distance between two adsorbed molecules). Assuming that

$$\Delta Q(\theta_1) = -\Delta\Phi(r)\big|_{r = r_0/\sqrt{\theta_1}}, \tag{85}$$

he obtained the equation

$$RT \ln[(1 - \theta_1)/\theta_1] - \Delta\Phi(r_0/\sqrt{\theta_1}) = RT \ln(1/p\sigma_1). \tag{86}$$

The solution of this equation for θ_1 with the specified $\Delta\Phi(r)$ interaction law yields the equation of the adsorption isotherm. In the region of very low and very high coverages, it is possible to neglect the second term in Eqn. (86). One then obtains the Langmuir isotherm [Eqn. (11)]. In the region of moderate coverages, the form of the adsorption isotherm depends on the interaction law. However, Vol'kenshtein does not consider the problem of the convergence of the sums expressing the interaction energy between the adsorbed molecules and their neighbours on the surface, which throws doubt on the validity of his conclusions§.

There has been a fairly large number of studies whose authors describe the repulsion of molecules from one another by statistical procedures such as the Bethe–Peierls [38,39] and Bragg–Williams [40] methods and the method of correlation functions [41]. In terms of the Bragg–Williams approximation, when the interaction between the molecules is taken into account by introducing an average molecular field, the adsorption isotherm is [40]

$$\theta/(1 - \theta) = ap \cdot \exp(z_1 J\theta_1/kT), \tag{87}$$

where z_1 is the number of adsorption centres on the surface closest to the given centre and J is the overlap integral (a constant).

Fedyanin [41] took into account the correlation between the adsorbed molecules, which was neglected in the Bragg–Williams approximation, and obtained the adsorption isotherm

$$\theta/(1 - \theta) = ap/[1 + ap\varphi(1/kT, z_1, J)], \tag{88}$$

where

$$\varphi(1/kT, z_1, J) = -z_1, [1 - \exp(J/kT)/1 + ap\exp(J/kT)]. \tag{89}$$

A novel idea concerning the nature of the long-range forces, leading to the repulsion of the adsorbed species, has been put forward by Breger and Zhukhovitskii [42]. Treating the electrons of the adsorbent as a Sommerfeld electron gas, they postulated that the electrons are

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‡ In the formulation of Eqn. (80) for the isotherm, there is a misprint in the paper of Kobozev and Gol'dfel'd [36] [Eqn. (10a)].

§ Pointed out by M. I. Temkin.

combined with the adsorbed species and are not involved in the motion of the remaining electrons forming the electron gas of the adsorbent. Thus adsorption results in the formation of nodes, the number of which increases as adsorption proceeds. The presence of the nodes increases the overall energy of the adsorbent electrons, which is manifested as the repulsion between the adsorbed species. The authors showed that such repulsion is inversely proportional to the distance and that, even with $r = 20$ Å, the repulsion energy is still 0.08 eV.

The electronic nature of the long-range forces in adsorption was assumed also in other investigations. Boudart[43] explained the decrease of the heat of adsorption with surface coverage on metals by the increase in the potential energy of the electrons due to the appearance of an additional potential jump in adsorption. He regarded the surface layer as a planar condenser with the charge uniformly distributed over the plates. Since for a given capacitance the energy of the condenser is proportional to the square of the charge, Boudart obtained a linear relation between the heat of adsorption and surface coverages. However, the "smearing" of the charge over the surface has been inadequately justified in physical terms.

In contrast to Boudart, Temkin[44] explained the decrease of the heat of adsorption with coverage by an increase of the kinetic energy of the electrons. He treated the layer of adsorbed atoms on the metal surface as a surface alloy, assuming that the electrons of the adsorbate atoms on the surface are combined with the free electrons of the surface metal atoms, forming a two-dimensional electron gas. The charge density at the surface increases, since the excess positive charge of the adsorbed atoms must be compensated. In the adsorption of an atom, there is a gain of some energy, part of which is evolved in the form of heat of adsorption and another part is used in increasing the kinetic energy of the electron gas. The treatment in such terms was carried out within the framework of the simplest Sommerfeld model on the assumption of a non-interacting electron gas. In contrast to the adsorption models postulating interaction between the chemisorbed species, which decreases with distance in accordance with some law, in the electron gas model the energy of the adsorbed layer depends only on the total number of adsorbed species but not on their relative positions. If the effective charge of the adsorbed species η is independent of θ_1, the adsorption energy is

$$\varepsilon = \varepsilon^0 - \eta^2 \frac{h^2N}{4\pi m^*}\theta_1, \tag{90}$$

where ϵ^0 is the value of ϵ corresponding to $\theta_1 = 0$, η is expressed in units of the elementary electric charge, h is the Planck constant, and m^* is the effective mass of the electron. The equation of the isotherm corresponding to Eqn.(90) is[45,46]

$$\ln ap = \frac{\eta^2h^2N}{4\pi m^*kT}\theta_1 + \ln\frac{\theta_1}{1-\theta_1}. \tag{91}$$

If the treatment is restricted to the first term of the expansion in Taylor's series of the second term on the right-hand side of Eqn.(91),

$$\ln\frac{\theta_1}{1-\theta_1} = 4\left(\theta_1-\frac{1}{2}\right)+\frac{16}{3}\left(\theta_1-\frac{1}{2}\right)^3+\dots+\frac{4^n}{2n-1}\left(\theta_1-\frac{1}{2}\right)^{2n-1}+\dots\P, \tag{92}$$

then Eqn.(91) is converted into Eqn.(57), with

$$f_1 = \eta^2\frac{h^2N}{4\pi m^*kT} \text{ and } a_0 = a\,e^2. \tag{93}$$

Fedyanin[47] estimated the contribution of the interaction of electrons to the overall kinetic energy of the electron gas. The theory of the mutual influence of adsorbed species was also investigated by Osherov[48], who considered the delocalisation of the wave functions of the electrons in the adsorbent crystal during adsorption.

V. POLYMOLECULAR ADSORPTION ISOTHERMS ON A HOMOGENEOUS SURFACE

If the pressure of the adsorbate vapour is close to the vapour pressure at the experimental temperature, the average thickness of the layer adsorbed on the surface of the adsorbent may exceed that of one molecule. As stated above, the adsorption isotherm for this case was obtained for the first time by Langmuir[11]. We shall now reproduce briefly Langmuir's derivation. Suppose that θ_0 is the fraction of the free surface and θ_{01}, θ_{02}, ... θ_{0n}, etc. are the fractions of the surface occupied by 1, 2, ..., n layers of adsorbed molecules. Then

$$\theta_0+\theta_{01}+\theta_{02}+\dots+\theta_{0n}=1. \tag{94}$$

The average degree of surface coverage by adsorbed molecules is

$$v/v_m = \theta_{01}+2\theta_{02}+3\theta_{03}+\dots+n\theta_{0n}, \tag{95}$$

where v_m is the degree of adsorption corresponding to the coverage of each site on the surface by one molecule. The rate of desorption of molecules from the nth layer is

$$\underset{\leftarrow}{r_n} = \beta_n'\theta_{0n}, \tag{96}$$

where β_n' is the rate of desorption of molecules from the nth layer when $\theta_{0n} = 1$. The rate of adsorption in the nth layer is

$$\underset{\rightarrow}{r_n} = \alpha_n'p\theta_{(n-1)}, \tag{97}$$

where α_n' is the rate of adsorption of molecules in the nth layer at the given pressure for $\theta_{n-1} = 1$. Having formulated the equilibrium conditions for each layer and using Eqns.(94) and (95), Langmuir obtained

$$\frac{v}{v_m} = \frac{a_1p+2a_1a_2p^2+3a_1a_2a_3p^3+\dots}{1+a_1p+a_1a_2p^2+a_1a_2a_3p^3+\dots}, \tag{98}$$

where $a_n = \alpha_n'/\beta_n'$. After dividing the numerator and denominator on the right-hand side of Eqn.(98) by the numerator, we obtain

$$\frac{v}{v_m} = \frac{a_1p}{1+Ap+Bp^2+Cp^3+\dots}, \tag{99}$$

where

$$\begin{gathered} A = a_1 - 2a_2, \\ B = a_2(4a_2 - 3a_3 - a_1), \\ C = 2a_2(6a_2a_3 - 2a_3a_4 + a_1a_2 - a_1a_3 - 4a_2^2). \end{gathered} \tag{100}$$

Eqn.(99) represents the adsorption isotherm for the case under consideration formulated in a general form. As a special case, Langmuir analysed the situation where $a_1 \neq a_2$, but $a_2 = a_3 = a_4 = \dots, a_n$. This corresponds to approximately identical adsorption capacities in all the layers except the first. After appropriate rearrangements, Eqn.(99) is converted into

$$\frac{v}{v_m} = \frac{a_1p}{(1-a_2p)(1-a_2p+a_1p)}. \tag{101}$$

¶ In Temkin's paper[46], there is a misprint in the formulation of the general term of the expansion.

Later Brunauer, Emmett, and Teller[49] assumed that the adsorption in all the layers other than the first takes place with a heat change equal to the heat of condensation E_Z. We then have in Eqn.(101)

$$a_1 = a_1^0 \exp(E_1/RT) \tag{102}$$

and

$$a_2 = a_2^0 \exp(E_L/RT). \tag{103}$$

After the notation

$$c = \frac{a_1^0}{a_2^0} \exp[(E_1 - E_L)/RT] \tag{104}$$

and

$$u = pa_2 \tag{105}$$

has been introduced, Eqn.(101) is converted into

$$v/v_m = cu/[(1-u)(1-u+cu)]. \tag{106}$$

It is seen from Eqn.(106) that $v \to \infty$ when $u \to 1$. Therefore and also on the grounds that $v/v_m \to \infty$ when $u \to 1$, Brunauer, Emmett, and Teller assumed that

$$u = p/p_0, \tag{107}$$

where p_0 is the vapour pressure over the liquid adsorbate.

It follows from Eqns.(103), (105), and (107) that

$$p_0 = 1/a_2^0 \exp(E_L/RT). \tag{108}$$

After substituting Eqns.(107) and (108) and algebraic rearrangements the following equation is obtained for the isotherm:

$$\frac{p}{v(p_0-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p_0}, \tag{109}$$

which is the equation of a linear plot of $p/v(p_0-p)$ against p/p_0. This equation is usually called the BET equation. It makes it possible to calculate the values of v_m and c when experimental data are available for the relation between v and p. If it is assumed that the area occupied by the adsorbed molecule of the given gas is constant and independent of the nature of the surface, then it is possible to determine the surface areas of adsorbents with the aid of Eqn.(109). This possibility is widely used in practice. The physical picture of adsorption constituting the basis of the derivation of the BET equation has been frequently discussed in the literature. It follows from Eqn.(104) that the coefficient c may be determined from the heat of adsorption in the first layer, provided that the ratio a_1^0/a_2^0 is known. In their publication[49], Brunauer et al. assumed that $a_1^0/a_2^0 = 1$. Then

$$c = \exp[(E_1 - E_L)/RT]. \tag{110}$$

However it has been shown, for example by Harkins and Boyd[50] and Beebe et al.[51], that c can be calculated from heats of wetting $E_1 - E_L$ or from calorimetric measurements of E_1, which are much higher than the values obtained from the BET isotherm when it is assumed that c is defined by Eqn.(110).

This may be due to three causes[52]. Firstly, a_1^0/a_2^0 may differ from unity. Secondly, the heat of adsorption in the second and succeeding layers may differ from the heat of condensation of the adsorbate, approaching it only gradually with increase of the number of adsorbed layers. Thirdly, in view of the inhomogeneity of the adsorbent surface, the BET equation is valid only in the region $\theta \gtrsim 0.5$, where the surface inhomogeneity does not have an appreciable effect. For this reason, the values of E_1 are calculated from the BET isotherm using data obtained for $\theta > 0.5$. As a result, one may expect that average values of E_1 will be obtained only for those molecules of the first layer which are adsorbed at sites with lower adsorption energies and not for the entire first layer. On the other hand, in the determination of the heats of wetting one obtains data averaged over the entire adsorbent surface. Statistical calculations have shown[53-55] that there are in fact no adequate grounds for believing that $a_1^0/a_2^0 = 1$ in the general case.

The second of these possible causes of disagreement between the values of c obtained in calculations from adsorption isotherms and from measurements of $E_1 - E_L$ was examined in detail by Clampitt and German[56]. These investigators based their treatment on the finding that, with increase in the thickness of the adsorbed film starting from two monolayers, the heat of adsorption of molecules from the gas phase to the film varies smoothly up to the heat of condensation. Using a method analogous to that described by Brunauer et al.[49], they derived an equation for polymolecular adsorption formally agreeing with the BET equation. The difference between these equations is that Clampitt and German[56] obtained

$$c = (a_1^0/a_2^0)\exp[(E_1 - 2E_L + E_S)/RT], \tag{111}$$

where

$$E_S = E_L - 1.35[RT + \gamma_0 (M/d)^{2/3}] \tag{112}$$

(γ_0 is the surface tension of the film and d the adsorbate density in the liquid state). In the next paragraph we shall return to the third cause of the disagreement between the values of c.

The problem of the validity of Eqn.(107), which is one of the principal components of the BET theory, has been frequently discussed in the literature. It has been stated (for example in Refs. 57–59), that there is no sufficient evidence for adopting this equation. It is more correct to assume that

$$u = p/g, \tag{113}$$

where $g \neq p_0$. The use of Eqn.(107) may be justified only because it can be derived from the simple equation of the BET isotherm, which can be readily used to determine the specific surfaces of solids.

When adsorption does not take place on a smooth surface but within the adsorbent pores whose diameter cannot be regarded as very large compared with the dimensions of the molecules, then there is a possibility of adsorbing a finite number of layers of adsorbate molecules on such a surface. An equation has been obtained for the polymolecular adsorption isotherm in pores bounded by two parallel planes[49], which, in contrast to the simple BET equation [Eqn.(109)], contains three parameters:

$$\frac{v}{v_m} = \frac{cu}{1-u} \cdot \frac{1-(n+1)u^n + nu^{n+1}}{1+(c-1)u - cu^{n+1}}, \tag{114}$$

where n is the number of adsorbed layers. When $n = 1$, this equation is converted into the equation of the Langmuir isotherm [Eqn.(11)] and, for $n \to \infty$, it is converted into the BET equation [Eqn.(109)].

The case where adsorption saturation is reached at pressures lower than p_0 has been investigated[60]. The authors suggested that this effect is associated with capillary condensation. By taking into account capillary condensation, equations were obtained for adsorption isotherms in which there is a fourth parameter, whose value depends on the heat of condensation of the adsorbent vapour, in addition to the parameters in Eqn.(114). These equations are extremely complex and have hardly any practical value.

VI. POLYMOLECULAR ADSORPTION ISOTHERMS ON INHOMOGENEOUS SURFACES

This equation of the BET isotherm [Eqn.(109)] can be used only in the range $0.05 < p/p_0 < 0.3$. One of the main causes of the failure of the BET isotherm for $p/p_0 < 0.05$ is surface inhomogeneity and, under the conditions where $p/p_0 > 0.3$, the interaction between the adsorbed molecules becomes significant. None of these effects can be taken into account by the BET theory. We shall consider the problem of the form of polymolecular adsorption isotherms on inhomogeneous surfaces. The first attempts to describe polymolecular adsorption processes on such surfaces were made by McMillan[61] and Walker and Zettlemoyer[62]. In these studies the surface was treated as a mixture of a finite number of adsorption centres with different adsorption energies. Then

$$v = \frac{u}{1-u}\left[\frac{v_{mA}c_A}{1+(c_A-1)u} + \frac{v_{mB}c_B}{1+(c_B-1)u} + \ldots + \frac{v_{mi}c_i}{1+(c_i-1)u}\right], \quad (115)$$

where c_A, c_B, ..., c_i and v_{mA}, v_{mB}, ..., v_{mi} are constants analogous to the constants c and v_m in Eqn.(109), which, however, refer to adsorption centres of types A, B, ..., i respectively. Eqn.(115) can be used to describe adsorption on an adsorbent consisting of a mechanical mixture of substances, each of which has a homogeneous surface.

The case where i is very large is more general. In order to obtained the adsorption isotherms on such a surface, simple summation must be replaced by integration. The integration requires that one specifies the law governing the distribution of sites on the surface with respect to heats of adsorption or standard Gibbs free energies of adsorption $\Delta G^0_{a_1}$. It is known from monomolecular adsorption data that the distribution of surface sites with respect to adsorption capacity can be usually described with the aid of a linear or exponential distribution law. The problem has been examined of finding the form of the polymolecular isotherms for any distribution of surface sites with respect to standard Gibbs free energies, when the monomolecular adsorption isotherm for the corresponding site distribution law is known[63].

The equation of the polymolecular adsorption isotherm can be put in the form

$$v = \frac{v_m c p}{(p_0-p)[1+(c-1)p/p_0]}, \quad (116)$$

and comparison of Eqns.(102), (103), (104), and (108) shows that

$$c = a_1 p_0. \quad (117)$$

Having substituted Eqn.(117) in (116), we obtain

$$v(1-u) = v_m \frac{a_1 p/(1-u)}{1+[a_1 p/(1-u)]}. \quad (118)$$

Comparison of Eqn.(118) with the equation of the Langmuir isotherm for monomolecular adsorption

$$v = v_m \frac{a_1 p}{1+a_1 p} \quad (119)$$

shows that the equation of the monomolecular adsorption isotherm can be converted into the equation of the polymolecular adsorption isotherm by replacing

$$\left.\begin{matrix} v \text{ by } v(1-u) \\ p \text{ by } p/(1-u) \end{matrix}\right\}. \quad (120)$$

and

The reverse conversion can be achieved by assuming that $p_0 = \infty$ in the equation of the polymolecular adsorption isotherm. If the surface is uniformly inhomogeneous, the monomolecular adsorption isotherm is described by an equation of type (62). Having replaced θ_1 by v/v_m and having substituted the variables in Eqn.(62) in accordance with Eqn.(110), we obtain the polymolecular adsorption isotherm on a uniformly inhomogeneous surface:

$$v = \frac{v_m}{f_1(1-u)} \ln \frac{1+a_0 p/(1-u)}{1+a_1 p/(1-u)}. \quad (121)$$

For a strongly inhomogeneous surface, where $a_0 \gg a_1$, in the region of moderate coverages Eqn.(121) becomes

$$v = \frac{v_m}{f_1(1-u)} \ln \frac{a_0 p}{(1-u)}. \quad (122)$$

In the case of an exponentially inhomogeneous surface, the adsorption isotherm has the following form in the region of moderate monolayer coverages under the conditions of polymolecular adsorption:

$$v = c\frac{p^\gamma}{(1-u)^{(1+\gamma)}}, \quad (123)$$

where

$$c = \frac{\gamma\pi v_m a_1^\gamma}{\sin \pi\gamma}. \quad (124)$$

Eqn.(123) can be obtained from the equation of the Freundlich isotherm, which describes monomolecular adsorption on an exponentially inhomogeneous surface at moderate coverages when the variables are substituted in accordance with formula (120).

In polymolecular adsorption, transition to the region of high surface coverages occurs already when $p/p_0 \simeq 0.05$. For this reason, in the case of polymolecular adsorption it is of interest to consider the adsorption not only in the region of moderate coverages but also in the region of high coverages. The equation of the adsorption isotherm for moderate and high surface coverages has therefore been obtained[64] by integrating the degrees of adsorption at sites with different adsorption capacities up to a minimal heat of adsorption in the first layer. When adsorption in layers above the first was considered[64], the same assumptions were made as in the derivation of the BET isotherm. The equation of the isotherm is

$$\frac{v}{v_m} = \frac{\pi\gamma \exp[E_L\gamma(h-1)/RT]}{\sin \pi\gamma} \cdot \frac{u^\gamma}{(1-u)^{(\gamma+1)}} - \frac{\gamma u \cdot \exp[E_L\gamma(h-1)/RT]}{(1-\gamma)(1-u)^2} \times$$
$$\times\left[1 - \frac{1-\gamma}{2-\gamma}\cdot\frac{u}{(1-u)} + \frac{1-\gamma}{3-\gamma}\left(\frac{u}{1-u}\right)^2 - \frac{1-\gamma}{4-\gamma}\left(\frac{u}{1-u}\right)^3 + \ldots\right], \quad (125)$$

where h is the ratio of the minimum heat of adsorption in the first layer to the heat of condensation E_L. For fairly small values of u, Eqn.(125) is converted into

$$\frac{v}{v_m} = \frac{\pi\gamma \exp[E_L\gamma(h-1)/RT]}{\sin \pi\gamma} \cdot \frac{u^\gamma}{(1-u)^{(1+\gamma)}}. \quad (126)$$

By taking logarithms in Eqn.(126), it is possible to obtain an expression which permits the determination of γ and h from a plot of $\lg[v(1-u)]$ against $\lg[u/(1-u)]$ using adsorption measurements in the region of fairly small values of u. The observed values of γ and h can then be used to describe the adsorption at high surface coverages using for this purpose Eqn. (125).[65] This makes it possible to determine whether or not the theory described above describes the experimental results.

By substituting Eqn. (107) in Eqn. (125) and assuming that $p_0 = \infty$, it is possible to obtain the equation of the monomolecular adsorption isotherm for moderate and high coverages corresponding to an exponential distribution of surface sites with respect to adsorption capacity.

VII. ISOTHERM FOR ADSORPTION IN MICROPORES

Adsorption by microporous adsorbents (i.e. adsorbents containing pores whose radius exceeds only slightly the size of the adsorbate molecules) at temperatures so low that dispersion forces are of decisive importance in the adsorption interaction constitute a special case. Langmuir did not consider it. We shall examine it in order to illustrate the view frequently encountered in the literature that the physical picture of polymolecular adsorption is not always adequate for the description of the adsorption of vapours when the amount adsorbed is greater than the volume of the adsorbate monolayer on the adsorbent surface. The theory of adsorption in micropores has been developed mainly by Dubinin and his coworkers[66,67]. It is assumed that micropores are filled at once and not layer by layer. The theory of the bulk saturation of micropores uses the temperature invariance of the characteristic adsorption equation noted by Polanyi. The characteristic adsorption equation is

$$\theta_1 = \exp[-(A'/E)^2]. \tag{127}$$

It is usually called the Dubinin–Radushkevich equation. Here θ_1 is the degree of bulk saturation of the adsorption space, E the characteristic adsorption energy (a parameter of the distribution function), and A' the differential molar work of adsorption, which is defined in the theory of bulk saturation of micropores as the decrease in the Gibbs free energy:

$$A' = RT\ln(p_0/p) \quad , \tag{128}$$

where p is the vapour pressure of the given substance in the standard state at a temperature T. The equation of the adsorption isotherm for the case under consideration can be formulated as follows[67]:

$$\theta_1 = \exp[-(A'/\beta E_0)^2], \tag{129}$$

where $\beta = E/E_0$ (E_0 is the characteristic adsorption energy for a standard vapour, benzene being usually employed as the standard. For adsorption in very small pores, where the adsorption interactions are strongest, the more general equation

$$\theta_1 = \exp[-(A'/E)^n], \tag{130}$$

where n is an integer, has been suggested[68] for the distribution function of θ_1 with respect to A'. Eqn. (127) can be regarded as a special case of Eqn. (130).

The theory of the bulk saturation of micropores is widely used to describe adsorption on activated charcoals, zeolites, microporous silica gels, etc.

VIII. CONCLUSION

The foundation of the modern theory of adsorption were laid by Langmuir in 1916–1918. The Soviet scientists Frumkin, Dubinin, Roginskii, Zel'dovich, Temkin, and others have contributed much to the development of the theory. The Langmuir, Freundlich, and Temkin isotherms are most widely used in studies on adsorption and the kinetics of heterogeneous catalytic processes and electrode processes (see for example, Refs. 14 and 69–71). The Dubinin–Radushkevich isotherm together with the Brunauer–Emmett–Teller isotherm, which is generally employed to determine the specific surfaces of solids, are extensively applied in the description of physical adsorption.

The above discussion permits the conclusion that the formal description of adsorption isotherms within the framework of Langmuir's fundamental postulates can now be regarded as largely completed. In certain cases the solutions may be refined. However, with present experimental techniques and the accuracy currently achieved in the results, refinements in the solutions cannot be of any practical value.

Apparently the most serious of the currently unsolved problems in the field under consideration is that of the quantitative elucidation of the physical causes of the inhomogeneity of catalysts and adsorbents. In this sense calorimetric studies and also studies of isotope exchange on catalyst surfaces are most promising. Methods for the investigation of surface inhomogeneity with the aid of measurements of the rates of isotope exchange have been developed and have been used successfully by Boreskov and the catalytic school of which he is the Head (see, for example, Refs. 72–74).

The problem of which physical (or physicochemical) parameters determine the nature of the distribution of surface sites with respect to adsorption capacity and of the quantitative expression of the relation between these parameters and the adsorption capacity is of special interest (in particular, it is not clear why experimental data frequently yield an exponent in the equation of the Freundlich isotherm close to 0.5). In other words, although adsorption isotherms can in fact successfully describe experimental data, the hypotheses concerning the distribution of surface sites with respect to adsorption capacity used in their derivation have no adequate physical justification at the present time.

In the adsorption of vapours on porous bodies, the observed surface inhomogeneity may be due to the presence of narrow pores. The heats of adsorption of vapours do not differ very greatly from the heats of their condensation, exceeding the latter usually by a factor of only 2–3 even in the region of low surface coverages. Thus the adsorption of vapours can be as a rule explained by the action of van der Waals forces. Since such forces are additive, the heats of adsorption of vapours in pores whose size is comparable to the size of the adsorbate molecules should be greater than on a smooth surface. In this case the distribution of surface sites with respect to heats of adsorption can be related functionally to the distribution of adsorbate pores with respect to radii. In the chemisorption of permanent gases, for example in the adsorption of oxygen or hydrogen at the usual temperatures of catalytic experiments, the heat of adsorption frequently exceeds the heat of condensation even by an order of magnitude. In such cases the decrease of the heats of adsorption with surface coverage can amount to tens of kcal mole^{-1}. This effect cannot be accounted for by the operation of van der

Waals forces. One of the possible causes may be the presence of impurities. However, the adsorption can be frequently described by the Freundlich isotherm, but it is not clear why the presence of impurities should lead so often to an exponential distribution of sites with respect to adsorption capacity.

We shall consider briefly the possibility of reaching conclusions concerning the nature of surface site distribution with respect to adsorption capacity or about the adsorption mechanism (for example, how many elementary areas on the surface are required for the adsorption of each molecule) solely on the basis of the form of the adsorption isotherm. In practice, adsorption isotherms are as a rule investigated over a fairly narrow pressure range (electrochemical studies in which the change of potential may correspond to a pressure change by a factor of 10^5 constitute an exception). In this case the possibility of describing the results with the aid of, for example, a power or logarithmic isotherm does not by itself demonstrate the validity of the corresponding distribution of surface sites with respect to adsorption capacity. In order to deduce the nature of the inhomogeneity, it is necessary to consider the isotherms together with the results obtained by other methods, for example the calorimetric method, the method of surface isotope exchange, the ESR method, studies of the kinetics of adsorption and desorption, etc.

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The Long-range Interaction between Colloid and other Particles and the Formation of Periodic Colloid Structures

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The general relations governing the formation of gel-like systems in electrolyte solutions have been formulated for particles of different size and shape. Comparison of the results of numerous experimental studies with data derived by theoretical analysis confirms the decisive role of long-range forces in the formation of periodic colloid structures and the extensive occurrence of these structures in nature and in technology. Peptisation, thixotropic processes, and syneresis as well as the phenomenon of reversibility in the formation of periodic colloid structures are examined and methods for estimating the interaction forces between dispersed particles are discussed on the basis of the rheological properties of periodic colloid structures.
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I. INTRODUCTION

By virtue of their unusual physicomechanical properties and characteristic capacity for thixotropic transformations, peptisation, and syneresis, periodic colloid structures (PCS), i.e. tactoids, heterogeneous gels, and gel-like systems, have for a long time attracted the continuous attention of investigators[1-9]. Examination of experimental and theoretical data established that the properties of disperse structures are to a large extent determined by the relative positions and orientation of the dispersed particles and also by the thickness of the liquid layers separating them[5-20]. Thus, over long quasiequilibrium distances (compared with atomic dimensions) between the particles, disperse structures consist of thixotropic and usually relatively unstable periodic colloid structures. However, when the particles stick together with retention of very thin liquid layers between them or when the adhesion process is accompanied by the appearance of direct contacts, fairly stable systems are formed, which have virtually no thixotropic properties and exhibit only a weak syneresis and a weak capacity for peptisation. Such relations have been observed, for example, for precipitates formed when metallic sols coagulate[21-23], for certain electrophoretic coatings[24], etc.

According to Rebinder's classification, thixotropic periodic colloid structures are reversible coagulation structures, while direct adhesion of particles and their further growth lead to the formation of irreversible condensation-crystallisation structures[14,25-27]. At the same time one must emphasise that the concept of periodic colloid structures is broader than that of coagulation structures and that not all periodic colloid structures (for example, equilibrium dispersions of swollen latex particles, micellar structures, etc.) can be classified as coagulations—thermodynamically non-equilibrium systems. The abundance of periodic colloid structures in nature and industry and their important role in various natural and industrial processes have been confirmed by the results of optical, X-ray diffraction, and electron microscope studies on a wide variety of disperse structures, including the results of direct observations on stabilised latex dispersions (Figs. 1 and 2).

The study of structure formation processes is associated with the development of concepts concerning surface forces of different types and acting over fairly long distances. The present advances in the theory of surface phenomena and also studies on coagulation (flocculation), gel formation, and the properties of gel-like systems have demonstrated the wide occurrence of long-range aggregation processes in which the characteristics of the particles and the relations governing their interactions are clearly manifested. In consequence of the predominance of attraction forces over long distances and the presence of a barrier preventing direct contact, in the mechanism of these processes the colloid particles are arranged in fixed relative positions with retention of liquid layers between them. On the other hand, in certain types of periodic colloid structures the fixation of particles is determined by the predominance of repulsion forces, as a result of which constrained conditions arise in the system.

The concept of the decisive influence of long-range interaction on the formation of thixotropic structures was put forward for the first time by Freundlich[28]. Subsequently many further experimental and theoretical studies led to its thorough confirmation, amplification and extension to a wide variety of classes of colloid structures[5-7]. This review discusses the principal results of such studies, which are being particularly vigorously prosecuted at the present time.

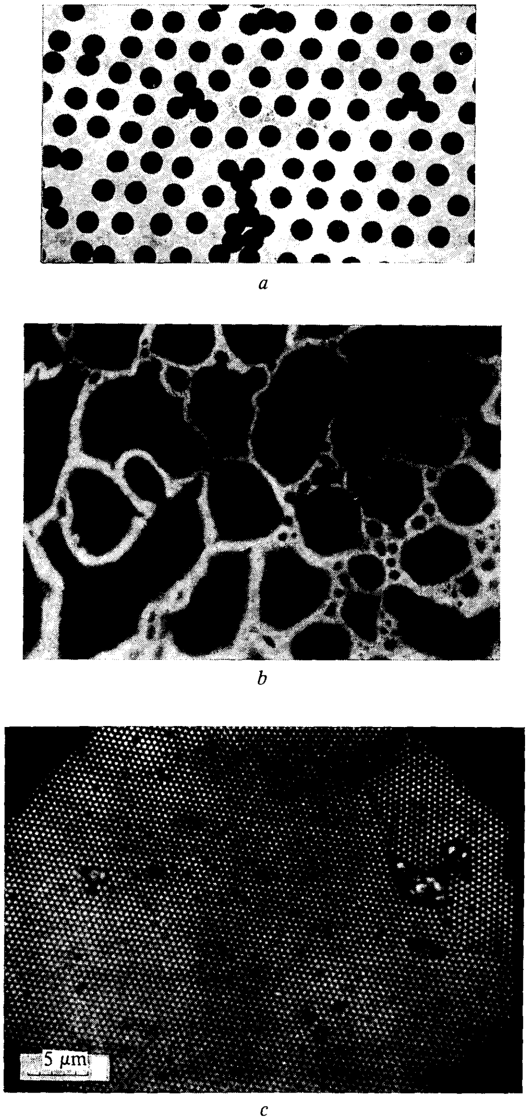

Figure 1. Electron photomicrographs of periodic colloidal structures: *a*) polystyrene latex with a particle radius of 950 Å; *b*) particles of epoxy-resin; *c*) particles of a styrene–butadiene copolymer with a radius of 1400 Å–lattice defects and dislocations are visible[11].

II. LONG-RANGE SURFACE FORCES

It is known that attractive forces (van der Waals–London forces, forces due to permanent electric and magnetic dipoles, and forces due to dipoles induced by the polarisation of ionic double layers) and ionic–electrostatic repulsion forces can act between particles. The fact that these are long-range forces is responsible for the probability of further aggregation, i.e. the fixation of particles at a secondary potential minimum (Fig. 3).

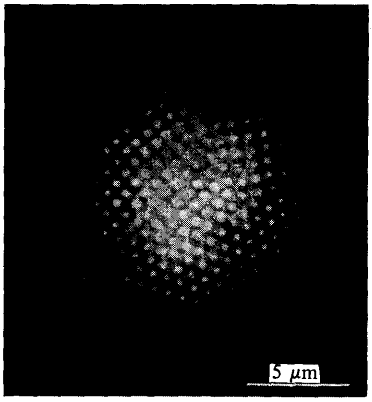

Figure 2. A photomicrograph of a polystyrene latex with a particle radius of 1700 Å for a solid phase concentration of 8 vol.%—the regions corresponding to the coexistence of the hexagonal and cubic lattices are clearly manifested[11].

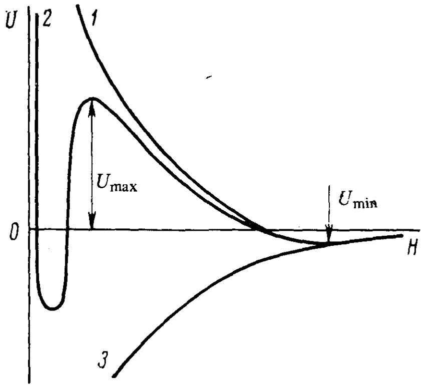

Figure 3. Various types of relations between the interaction energy of the dispersed particles and the distance between their surfaces.

Apart from molecular and dipole attraction forces as well as ionic–electrostatic repulsion forces, forces of a different type can also be manifested in the formation of periodic colloid structures.

Forces Due to the Viscoelastic Resistance of Anomalous Liquid Layers

Such forces offer resistance both to the mutual approach of the surfaces and to their separation from one another and, like ionic layers, influence the occurrence of a secondary minimum on the interaction energy curve for the particles[5,29–32]. The unusual relation between the disjoining pressure and the thickness of the film wetting the surface of quartz was recently explained in terms of the structural component and the three-layer model of a polar liquid film (presence of a layer with enhanced enthalpy or the so called partially fused layer)[33,34].

Forces Resisting the Rupture of Adsorption Layers Containing Surfactant or Polymer Molecules

The interaction between surfaces stabilised by adsorption layers (steric and entropy factors) has already been discussed[35-43].

One must also take into account the following factors: the thermal (Brownian) motion of particles[44-49]; gravitational[50,51], and centrifugal[52,53] forces which frequently appear to be equivalent to attraction forces and promote structure formation; mechanical compressive forces[29,54-55] and hydrodynamic[56-58] and capillary forces[59-62], which frequently have a marked influence on the properties of disperse and capillary-porous systems, as well as inertial, mirror image, and other forces[58].

Intermolecular van der Waals–London Forces

Despite the significant defects of the London–Hamaker microscopic theory[63], its equations are still widely used. The attraction energy between two identical spherical particles with a radius a and a distance R between their centres is given by the following expression when no account is taken of electromagnetic retardation:

$$U_m = -\frac{A}{6}\left(\frac{2a^2}{R^2-4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2-4a^2}{R^2}\right), \tag{1}$$

where A is the Hamaker constant; for low values of $H = R - 2a \ll a$ (H is the shortest distance between the interacting surfaces), we have

$$U_m = -\frac{A}{12}\left(\frac{a}{H} - 2\ln\frac{a}{H}\right), \tag{2}$$

or in a still simpler form

$$U_m = -Aa/12H. \tag{2$'$}$$

The corresponding formulae where account is taken of electromagnetic retardation were obtained by Schenkel and Kitchener[64] and for two spheres with radii a_1 and a_2 by Wiese and Healey[65]. Similarly, for $H \ll a_1$, a_2, we have[66]

$$U_m = -Aa_1a_2/6H(a_1 + a_2). \tag{3}$$

For two identical plates with a thickness b and a separation H, the expression is[20,67]

$$U_m = -\frac{A}{12\pi}\left[\frac{1}{H^2} + \frac{1}{(H+2b)^2} - \frac{2}{(H+b)^2}\right]f(H), \tag{4}$$

where $f(H)$ is a function taking into account the electromagnetic retardation; its value for different H can be determined from tables and the graph quoted in Kruyt's book[67] and in the monograph of Sonntag and Strenge[36].

When $H \ll b$, we have

$$U_m = -\frac{A}{12\pi H^2}. \tag{5}$$

All these formulae are valid on the assumption that the interacting bodies are *in vacuo*. Allowance for the influence of liquid layers usually reduces to finding the effective Hamaker constant; the following simple relation is then frequently used[58,63]:

$$A = (\sqrt{A_{11}} - \sqrt{A_{22}})^2, \tag{6}$$

where A_{11} and A_{22} are constants for the particles and the medium *in vacuo*. However, Eqn. (6) is not rigorous[68] and, when the values of A_{11} and A_{22} are similar, the calculation leads to considerable errors.

The principal defects of the microscopic theory are as follows: (1) the applicability of the law of interaction of gas particles to condensed bodies is postulated; (2) the complete additivity of the electronic interactions is assumed; (3) the summation of such interactions over short distances between bodies is replaced by integration with respect to volume. The macroscopic theory of the intermolecular interaction of condensed bodies[69], based on the analysis of electromagnetic field fluctuations, is free from these defects. Dzyaloshinskii, Lifshits, and Pitaevskii[70,71] took into account the influence of the dispersion medium.

According to the macroscopic theory, the solutions of the problem of the interaction of bodies via a liquid layer assume a simple form for distances H which are both large and small compared with $\lambda_0/2\pi$ (λ_0 is the fundamental length in the absorption spectrum or the London wavelength). The following expression has been obtained for the force of the interaction between two plane-parallel particles *1* and *2* via a liquid layer *3* for large values of $H \gg \lambda_0/2\pi$ (for dielectrics, $\lambda_0/2\pi \simeq$ 20–30 nm):

$$P_m = \frac{3\hbar c}{16\pi^2 H^4\sqrt{\varepsilon_{30}}}\int_1^\infty\left[\frac{s_{10}-p)(s_{20}-p)}{(s_{10}+p)(s_{20}+p)} + \frac{(s_{10}-\alpha p)(s_{20}-\beta p)}{(s_{10}+\alpha p)(s_{20}+\beta p)}\right]\frac{dp}{p^2}, \tag{7}$$

where $s_{10} = (p^2 - 1 + \alpha)^{1/2}$, $s_{20} = (p^2 - 1 + \beta)^{1/2}$, $\alpha = \epsilon_{10}/\epsilon_{30}$, $\beta = \epsilon_{20}/\epsilon_{30}$ (ϵ_{10}, ϵ_{20}, and ϵ_{30} are the static dielectric constants of the plates and the liquid layer), $\hbar = h/2\pi$ is the Planck constant, c the velocity of light, and p the parameter with respect to which the integration is carried out.

Calculations based on Eqn. (7) can be carried out by a graphical procedure. The accuracy of the calculations is in many instances determined primarily by the appropriate choice of the static dielectric constants.

For two identical plates, $\epsilon_{10} = \epsilon_{20}$ and Eqn. (7) simplifies to

$$P_m = \frac{\hbar c\pi^2}{240H^4\sqrt{\varepsilon_{30}}}\left[\frac{\varepsilon_{10}-\varepsilon_{30}}{\varepsilon_{10}+\varepsilon_{30}}\varphi\left(\frac{\varepsilon_{10}}{\varepsilon_{30}}\right)\right]. \tag{8}$$

The function $\varphi(\epsilon_{10}/\epsilon_{30})$ has been calculated by Lifshits[69] and the calculation for $\epsilon_{10} \neq \epsilon_{20}$ has been carried out by Devereux and de Bruyn[72]. For two metallic plates in a medium with a dielectric constant ϵ_{30}, the function $\varphi(\infty) = 1$, since $\epsilon_{10} = \epsilon_{20} = \infty$. Then

$$P_m = \frac{\hbar c\pi^2}{240H^4\sqrt{\varepsilon_{30}}}. \tag{9}$$

The same equation was obtained by Casimir[73,74] on the basis of the microscopic theory with $\epsilon_{30} = 1$.

Integration of Eqn. (8) leads to an expression for the attraction energy between two plates at a distance of 1 cm:

$$U_m = -\frac{\hbar c\pi^2}{720H^3}\left(\frac{\varepsilon_{30}-1}{\varepsilon_{30}+1}\right)\varphi(\varepsilon_{30}), \tag{10}$$

or

$$U_m = -\frac{K}{H^3}, \tag{11}$$

where K is the constant of the molecular attraction forces over long distances.

Using Deryagin's transformation[75], the formula for the attraction energy between two spheres can be obtained from Eqn. (11):

$$U_m = -\frac{\pi K a}{2H^2}. \tag{12}$$

For two plates with $H \ll \lambda_0/2\pi$, we have

$$P_m = \frac{\hbar}{16\pi^2 H^3} \int_0^\infty \int_0^\infty x^2 \left[\frac{(\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)}{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)} \exp x - 1 \right] \mathrm{d}\,x\,\mathrm{d}\,\xi. \qquad (13)$$

Neglecting unity compared with the term containing $\exp x$ and integrating with respect to x, we obtain

$$P_m = \frac{\hbar}{8\pi^2 H^3} \int_0^\infty \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)} \,\mathrm{d}\,\xi, \qquad (14)$$

where ϵ_1, ϵ_2, and ϵ_3 are the dielectric constants as a function of the imaginary frequency $i\xi$. It follows from the above equation that the sign of the molecular interaction force is determined by the values of ϵ_1, ϵ_2, and ϵ_3. One must assume that, when the interacting surfaces approach one another, the sign of the quantity P_m may be reversed as a result of the different changes in the complex dielectric constant in them layers.

The microscopic and macroscopic theories of molecular forces yield [virtually] identical relations for the attraction forces *in vacuo* as a function of distance, differing only in the values of the constants. The experimental characteristics agree best with calculations based on the macroscopic theory[76–81].

The long-range nature of the molecular forces in condensed systems has been confirmed by the direct measurements of Abrikosova and Deryagin[76–81] as well as other investigators[82]. Many important studies have been made recently on the further development of the macroscopic theory, the improvement of the microscopic theory, and the development of methods for the calculation of the intermolecular attraction constants. This is because direct calculations of the forces of interaction via liquid layers are very complicated and have been carried out on the basis of Lifshits's theory for the simplest case of plates infinite in extent and separated by a planar gap the size of which must correspond to the limiting conditions ($H \gg \lambda_0/2\pi$ or $H \ll \lambda_0/2\pi$).

Van Kampen and coworkers[83–85] proposed a simpler method for the calculation of molecular forces equivalent in its approach to the Lifshits method; they considered the interaction between harmonic oscillators located at the interface. Using this method, Mitchell and Ninham[86] obtained the following expression for the attraction energies between two identical spheres in a liquid medium (for $H \ll a$):

$$U_m = -\frac{1}{12}\left(A_1 \frac{a}{H} - 2A_2 \ln \frac{a}{H}\right), \qquad (15)$$

where A_1 and A_2 are constants.

For $A_1 = A_2$, this equation is transformed into Hamaker's equation [Eqn. (2)] [when the particles and the dispersion medium have similar spectroscopic characteristics (for example in the case of quartz and mica particles in water)]. For semiconductor and particularly metal dispersions in liquid dielectrics, A_1 and A_2 must differ significantly, so that Eqns. (1) and (2) cannot be used. Muller and Churaev[87] calculated the values of U_m for particles of metal hydrosols on the basis of the macroscopic theory using the spectroscopic characteristics of water and the metals. Churaev[88–90] calculated the molecular components of the disjoining pressure in terms of Lifshits's theory for thick and thin wetting films of non-polar liquids. On the basis of a number of simplifying assumptions, he obtained recently an equation for the dependence of the molecular forces on distance for the entire range of film thicknesses and he also calculated the dispersion interaction forces in the transitional region[91]. A satisfactory agreement was achieved between the results of the calculations and experimental data.

The good agreement between the calculations based on Lifshits's theory and experimental molecular force constants has been pointed out in a number of interesting studies[69–81, 92–98]. On the basis of the analysis of the equations of the macroscopic theory, Churaev[99] showed that Hamaker's constants for the interaction via a liquid layer cannot be obtained by the summation of the constants for the interaction *in vacuo*. The results of the calculations of the attraction forces between identical bodies via a liquid layer exhibit appreciable discrepancies for both theories.

Taking into account double and triple correlations, Renne and Nijboer[100] derived approximate formulae for the atom–wall and two plane-parallel plate models. The studies of Rusanov and coworkers[101–104] and other investigators[105–107] were devoted to the solution of the problem of the molecular interaction between colloid particles in a liquid dispersion medium. The problem of the interaction of coaxial cylindrical and concentric spherical surfaces has been solved[108] on the basis of Lifshits's theory. A number of studies[109–111] were devoted to problems of the shielding of van der Waals forces in electrolyte solutions. The influence of the molecular condenser (Stern layer) on the overall interaction forces between colloid particles and on the stability of sols has been examined by Martynov and Muller[112, 113].

The Interaction Forces between Colloid Particles with Permanent Electric Dipole Moments

Studies on colloid solutions in the field of rectangular pulses (π-field) and in a rotating electric field (B-field) have shown that in many cases the colloid particle is a permanent electric dipole[114–119] due to the spontaneous unipolar orientation of the polar molecules (ions) adsorbed on the surface of the particle[114, 115]. Measurement of the relaxation times for the orientation of the particles in the π-field and the determination of the angle by which the dichroic axis of the particle deviates from the direction of the B-field make it possible to calculate the dipole moment μ_p. The values of μ_p for various colloid particles amount to hundreds of thousands and millions of debyes[115].

The data compiled in Table 1 [120] demonstrate the surface nature of the dipole, the results being confirmed by the results of electron-optical studies on other suspensions and sols, for example the sols of various modifications of HgS. At the same time, these data do not of course constitute proof of the impossibility of the bulk-phase nature of the rigid dipole, which may arise as a result of the spontaneous orientation of the polar groups of the material of the disperse phase.

Identical particles of ferromagnetic materials behave similarly to the dispersed particles of dielectrics with permanent dipole moments[121–123].

The Interaction Forces between Induced Electric Dipoles

The deformation of the ionic double layer (DL) occurring under the influence of a particular factor produces an electric field with a radius of action of the order of the size of the dispersed particles, leading to their long-range interaction. The polarisation of the DL plays an important role in the electrophoretic precipitation of suspensions, determining the quality of the coating, in the electrical treatment of cement pastes, electromelioration, vibrocondensation of dispersed materials, etc.

An approximate formula has been derived for the induced dipole moment[124,125]:

$$\mu_i = \frac{6a}{\sqrt{\pi}}\left[\left(\frac{\zeta\varepsilon_{\text{д}0}}{2} + \frac{zeb_i}{3r_e}\right)\frac{\zeta\varepsilon_{\text{д}0}r_e}{\Theta\varkappa^2}\right]E, \tag{16}$$

where ζ is the electrokinetic potential, z and r_e are the valence and the effective radius of the counterions, e is the electronic charge, b_i a coefficient taking into account the anomalous mobility of the counterions, E the external electric field strength, and Θ the product of the Boltzmann constant and the absolute temperature. Eqn. (16) was obtained from the expression for the energy of the polarisation interaction derived using the insufficiently reliable Stauff formula[126], which does not take into account the tangential fluxes of the diffuse-layer ions.

Table 1. The molecular dipole moments (μ_p^0) of the liquid medium and specific (per cm^2) dipole moments (μ_p^s) of diamond (in CGSE units).

Dispersion medium	$10^{18}\mu_p^0$	$10^{14}\mu_p^s$	Dispersion medium	$10^{18}\mu_p^0$	$10^{14}\mu_p^s$
Water	1.85	1.7	Ethyl acetate	1.88	0.10
Methyl alcohol	1.64	1.1	Propyl acetate	1.88	0.12
Ethyl alcohol	1.70	1.1	Acetone	2.72	1.03
Propyl alcohol	1.59	1.1	Cyclohexanone	2.80	0.36
Butyl alcohol	1.64	1.1	Ethyl methyl ketone	2.75	0.82
Isobutyl alcohol	1.79	1.1	4-Methylisobutyl ketone	2.73	1.05
s-Butyl alcohol	1.70	1.1	Nitrobenzene	3.99	0.90
t-Butyl alcohol	1.66	1.1	Nitromethane	3.20	1.80
Pentyl alcohol	1.66	1.1	Acetonitrile	3.37	0.98
Dioxan	0.21	0.82	Dimethylformamide		0.43
Chlorobenzene	1.56	0.17	Acrylonitrile	3.40	1.26
Bromobenzene	1.53	0.16	Dimethyl sulphoxide	4.30	1.35
Methyl acetate	1.64	0.22			

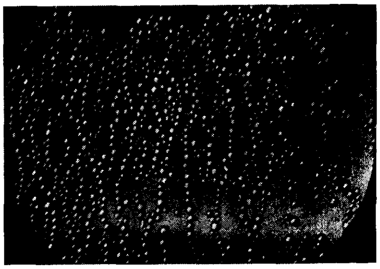

Figure 4. A photomicrograph of the aggregates formed in the latex under the influence of an external electric field.

The interaction of the induced dipoles usually leads to the appearance of chain aggregates (Fig. 4), which was first noted by Muth[127] and was subsequently studied in detail by many investigators[128-132]. Dukhin and coworkers[133-139] as well as other investigators[140-145] have made a major contribution to the development of concepts concerning the DL polarisation.

The following correct formula for the dipole–dipole interaction between two spherical particles has been proposed[139]:

$$V_{ip} = -4\varepsilon_{30}E^2B^2\frac{a^9}{(2+H/a)^3}, \tag{17}$$

where $B = \frac{1}{2} - 3[\cosh(u_1/2) - 1]/[4\cosh(u_1/2) + \kappa a]$ and u_1 is the dimensionless potential of the Stern layer. In addition, the overall interaction energy of these particles in an external electric field was calculated. The energy of the overlapping of the ionic double layer was determined from the equation derived without restriction to the value of the u_1 potential[146].

The Ionic-Electrostatic Repulsion Forces Between Surfaces

These arise when diffuse ionic layers having identical charges overlap[147-158]. In some studies[148-152], the system of interacting ionic double layers is treated with some degree of approximation as corresponding to equilibrium and the corresponding forces are referred to as the equilibrium electrical surface forces. They are governed by the change in the energy density of the electrostatic field[152] and also by the variation of the chemical potentials of the ions and the solvent in the gap between the surfaces which have approached one another[5].

In recent studies undertaken to develop further the DL theory, account has been taken of the influence of the intrinsic volume of the ion and of pair correlations on the DL structure[159], of the DL polarisation on electrophoresis and diffusiophoresis[160], and of adsorbed ions on the DL structure and polarisability[161]; problems concerning the discrete nature of the DL, [162] the determination of the surface potential of the spherical particles[163], and the comparison of the constant surface potential and constant surface charge conditions in the Deryagin–Landau–Verway–Overbeek (DLVO) theory of the stability and coagulation of colloids[164] have also been examined. In addition the results of studies on the interaction of DL-charged surfaces have been published: in a solution of a mixture of electrolytes[165,166]; for planar particles in concentrated dispersions[167]; for spherical particles in concentrated dispersions containing a dispersion medium with a low dielectric constant[168]; for planar and spherical particles in an aqueous medium[169]; at constant surface potentials[170] and surface charges[65,171,172] and also at a constant potential of one surface and a constant charge of another[173,174]; for surfaces with energetic and geometrical inhomogeneities[175-177]. Calculations have been made on the DL interaction over long distances[165,166,178] and an equation has been proposed which can be used for weakly charged surfaces[178]:

$$U_i = \frac{\varepsilon_{30}\psi_0^2 a(R-a)}{R}\ln\left\{1 + \frac{a}{R-a}\exp[-\varkappa(R-2a)]\right\}, \tag{18}$$

where R is the distance between the centres of the particles, ψ_0 the surface potential, and κ the Debye parameter.

A formula has also been obtained for the calculation of the energy U_i in the interaction of two similar spheres over long distances (for $\kappa a \gg 1$) without limitation as regards ψ_0. [146]

An interesting attempt has been made in a number of studies to examine from a single standpoint the energy of the interaction (the van der Waals attraction and the electrostatic repulsion energies) of charged surfaces.

Here a joint study was made of the low-frequency electromagnetic fluctuations and of the statistical charge distribution between two plates[179,180] and account was taken of the influence of the dielectric constant of the medium on the energy of the ions located near the interface[181]. The image method has been used[182] to calculate the interaction energy of two dielectrics *1* and *2* of different types separated by a layer of a dielectric *3*.

The dependence of the dimensionless potential u_1 of the Stern layer on the electrolyte concentration and the specific adsorption of the ion was studied recently[183]. It was concluded that the relation

$$n_c z^6 = \text{const}, \tag{19}$$

(where n_c and z are the critical concentrations and the valence of the counterions), established by Deryagin and Landau for dimensionless potentials $u_1 \geqslant 10$, should hold for arbitrary identical surface charges.

For different surface charges, the overlapping of ionic layers causes the mutual approach of the particles. For the same sign of the surface charges, but somewhat different potentials, the ionic-electrostatic forces P_i determine the repulsion of the particles over comparatively long distances and their attraction over short distances. The height of the maximum on the $P_i = f(H)$ curve depends on the lowest potential[184-186]. The interaction of the DL of inhomogeneous plates with different but constant charge densities has been studied[187], while another investigation[188] has dealt with the interaction of two plates immersed in ideal and non-ideal electrolyte solutions.

We may note that, as for molecular forces, the theoretical relations governing the action of surface ionic-electrostatic forces have been subjected to extensive experimental tests, the results of which basically confirmed their validity[29,36,37,147,189-196].

III. THE FIXATION OF PARTICLES AT A SECONDARY POTENTIAL MINIMUM AND THE FORMATION OF LOCAL PERIODIC COLLOID STRUCTURES

Under certain conditions, there is a fairly deep distant minimum on the curve for the interaction energy of colloid particles, $U(H) = U_m(H) + U_i(H)$, which determines the possibility of the mutual fixation of the particles with retention of the liquid layer between them. The probability of further aggregation and the lifetime of the aggregate formed depend on the depth of the minimum $U_{\min}$ and on the height of the potential barrier $U_{\max}$, which reduces the frequency I of the effective collisions[66,197-199], as a result of which the particles are fixed at the primary minimum (short-range aggregation):

$$I = \frac{16\pi DaN}{2\int\limits_2^\infty \exp(U/\Theta)\,\mathrm{d}\,s/s^2} \simeq \frac{16\pi DaN}{\frac{1}{2\varkappa a}\exp(U_{\max}/\Theta)}, \tag{20}$$

where N is the numerical concentration (the number of particles per unit volume) and D the diffusion coefficient.

The fixation of particles at a secondary minimum has been observed by numerous investigators[5-7] and confirmed by the results of many studies undertaken recently and designed to investigate the influence on the further aggregation of electrolytes[112,113,200-211] of the size, shape, and concentration of the colloid particles[5,65,212-217], and of the external force fields—electrical[124-128,139,218-223], magnetic[121,224-226], gravitational[50,51], centrifugal[52,53] hydrodynamic[56-58,227], etc.

A long-range interaction frequently occurs in processes involving the adhesion of the dispersed particles to a solid surface in the liquid medium. This has been confirmed by numerous experimental data[228-243]. Thus, when particles are deposited in air and also on a support in a liquid, the force required to strip them off, which is equal in absolute magnitude to the force of adhesion, is as a rule much greater in the former case[244-246]. Evidently the fixation of the particles at long distances corresponds to lower adhesion forces, while on deposition in air and the subsequent maintenance of the test specimens in the dispersion medium there are either no liquid layers between the particles and the macrosurface or their thickness is very low.

The theory of the collective interaction of particles has not as yet been duly developed. Therefore, in considering the problems associated with the formation and properties of periodic colloid structures, one usually begins with the relations governing the variation of the pair potential as a function of distance.

The Influence of Electrolytes on Long-Range Aggregation Processes

According to the DLVO theory, an increase of electrolyte concentration in the dispersion medium causes a contraction of the diffuse component of the DL and a decrease of the repulsion barrier. At the same time there is an increase in the depth of the secondary minimum $U_{\min}$ and a corresponding increase of the probability of long-range aggregation of particles, which is proportional to $\exp(U_{\min}/\Theta)$.

Table 2. The exponents ν in the equation nz^ν = const. for long-range aggregation processes.

Sol	ν	References	Sol	ν	References
V_2O_5	2.1—2.5	248	Latexes (a, μm):		
$Fe(OH)_3$	3.0—3.3	248	Polyacrylonitrile		
$Fe(OH)_3$	3.1	249	0.1	2.6—4.8	210
SiO_2	2.4	250	Polystyrene		
SiO_2	2.8	251			
CeO_2	4.3	252	0.1	3.3	261
H_2WO_4	2.0	253—255	0.19	3.3	200
S	3.0	256	0.17	3.2	212
S	3.6	257	0.21	3.4	212
AgI *	2.0	258	0.38	3.4	212
Au	2.7	259	0.54	3.5	212
Au	2.0	260	0.69	3.4	212
Ag	2.0	260	5.0	3.2	64
Cu	2.0	260	Polycaproamide		
			10	3.0	262
			Emulsions	3.1—3.3	203, 247

*Sol stabilised by poly(vinyl alcohol).

It has been known for a comparatively long time on the basis of experimental findings that gel-formation occurs at lower electrolyte concentrations than coagulation and the valence of the ions has a significant influence on the amount of electrolyte necessary for gel formation[247]. This relation has been demonstrated theoretically in studies[201,202] dealing with the interaction of two infinitely large plates and two spherical particles immersed in a symmetrical electrolyte.

It has been shown that, for a constant depth of the secondary force minimum, the following relation holds for the concentration and valence of counterions over a wide range of variation of the potential u_1:

$$nz^{2.5} = \text{const}, \tag{21}$$

and, when the effect of electromagnetic retardation for molecular forces is taken into account, we have

$$nz^{3.5} = \text{const}. \tag{22}$$

Both the limiting equations (21) and (22) and the intermediate equations with power exponents in the range 2.5–3.5 apparently hold in long-range aggregation processes.

The rate of gel formation and the stability of the gel usually depend on many factors (polydispersity, the presence of impurities, etc.), which are frequently difficult to take into account and this makes it difficult to obtain reliable results. For this reason, the relations between the valence and concentration of ions, derived from the results of many investigators and illustrated in Table 2, are approximate and depend on the methods used for the experimental determination of the PCS characteristics.

The concentrations of electrolytes required for coagulation and gel formation are compared in Table 3. Similar data were obtained by Kratochvil et al.[263] in a study of sols of microcrystalline cellulose and by Aleksandrova and Mochalova[264], as well as other investigators[265-268].

Table 3. The concentrations of electrolytes in the coagulation of an Fe_2O_3 sol and its conversion into a gel[28].

Content of disperse phase, g litre^{-1}	4,92	52,6
Electrolyte	Coagulation threshold, mmole litre^{-1}	gel-formation threshold, mmole litre^{-1}
NaCl	325.0	45.0
KCl	350.0	45.1
KBr	500.0	62.0
Na_2SO_4	3.25	12.0
$Na_2(COO)_2$	2.75	9.5
ν	7.1	2.3

Thus the results of the experimental investigation of the gel-formation processes in sols are consistent with the conclusions reached from the theoretical examination of the dependence of the depth of the secondary minimum on the concentration and valence of the ions. Calculation of the values of ν in the relation nz^{ν} = const. can evidently yield information about the type of aggregation: ν = 6–7 for short-range coagulation and ν = 2.5–3.5 for long-range aggregation.

It has been shown[268] that, when the dispersed particles are fixed at long distances from the macrosurface, Eqn. (21) also holds; together with Eqn. (22), it must be regarded as a general criterion of the influence of electrolytes on long-range aggregation processes.

At the same time it follows from the analysis of Table 3 that the aggregation of particles is greatly influenced both by the concentration of the electrolyte in the system and by the concentration of the disperse phase. Thus it has been established[249] that, for an Fe_2O_3 concentration of 13.05 g litre^{-1} and a specific KCl consumption equal to 1.532×10^{-3} mole g^{-1}, the sol becomes turbid, the process being accompanied by local gel formation. Subsequently, with increase of the specific consumption of KCl, the individual gel-like regions are combined, giving rise to a thixotropic structure throughout the entire volume of the sol, which then breaks down owing to the short-range coagulation of the particles.

The Influence of the Size and Shape of the particles on their Mutual Fixation at Long Distances

Processes involving the formation of gel-like systems depend on the size and shape of the particles[5,65,212-217], which can be explained by taking into account quantitatively the forces operating in the system.

The interaction of homogeneous plates of different thicknesses for the same values of the parameters characterising their molecular attraction and ionic-electrostatic repulsion energies has been studied[20] and it has been shown that the rate of aggregation of large particles with one another and with small particles should be greater than the rate of the short-range coagulation of small particles. This conclusion has been confirmed by an experimental study of the kinetics of the formation of aggregates in suspensions[269]. At the same time the probability of the long-range aggregation of thick plates is higher than that of thin plates, since in the latter case the depth of the secondary energy minimum is smaller. Such relations have been noted in studies of gel formation in a number of disperse systems[270-274]. It has been established that a liquid is formed in gel formation primarily between large planar particles, while small particles remain predominantly in a free state and during syneresis are separated together with the syneretic liquid.

The method developed[20,45,46] for plotting curves characterising the interaction energy of three plates as a function of their relative positions made it possible to examine the influence of the concentration of the disperse phase on the short- and long-range aggregation processes[5]. It has been shown, that for fairly long distances between the surfaces, both thin and thick plates resist direct aggregation. This corresponds to a low bulk-phase (or weight) concentration of small planar particles and a high concentration of large particles. With increase of the content of the disperse phase, the distances between the surfaces and hence the resistance to aggregation diminish more sharply for thin plates, which is the reason for their coagulation at concentrations in the range where coarsely disperse systems can still be stable.

Consideration of potential curves for the interaction of three particles made it possible to explain qualitatively a number of the characteristic features of coagulation and gel formation in highly and weakly disperse colloid solutions. For example the rapid decrease of the depth of the minimum with increase of the content of thin plates is responsible for the difficulty of obtaining concentrated gels from highly disperse sols and, even if such gels are formed, rapid syneresis is their characteristic feature, as for gels containing coarsely dispersed particles. The interaction of plates of different types and dimensions is analogous although more complex.

In contrast to plates, the height of the ionic-electrostatic barrier and hence the resistance to aggregation of spherical particles increase with increase of their size (Fig. 5). In particular, this factor has been used by Oden[275] to fractionate sulphur sols. At the same time a fairly deep secondary energy minimum has been observed for large spherical particles and for large particles of other shapes. For this reason, long-range aggregation processes should be particularly common in coarsely disperse systems[67]. This is confirmed by the existence of many concentrated periodic colloid structures, for example pastes, capable of peptisation and thixotropic transformations. Cement solutions (in the initial period of solidification)[276,277], silica[278-280] and Prussian Blue[274] gels, gel-like sulphur deposits[256], etc.

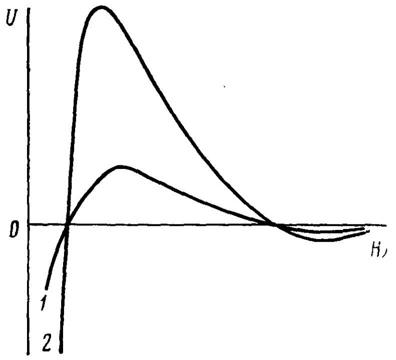

Figure 5. Dependence of the interaction energy of small (curve *1*) and large (curve *2*) spherical particles on the distance between their surfaces.

Furusawa and coworkers[212] investigated the aggregation of spherical polystyrene particles in different narrow fractions and established that, in the electrolytic coagulation of the most coarsely disperse system, the aggregation of particles occurs as a result of their fixation at a secondary minimum, because the stability of the system is restored after the removal of the electrolyte. Wiese and Healey[65] constructed a diagram (Fig. 6) where regions corresponding to the stable state of the system (region I) and to the unstable state leading to coagulation at the primary (region II) and secondary (region III) minima were defined as a function of the concentration of ions and the ratio of the radii of the particles. In the calculations, the dimensions of the particles, the surface charge, and other parameters were varied.

In connection with the wide occurrence of polydisperse systems, the question of interaction of particles of different size assumes particular importance. It has been shown[215] that fixation of small particles at long distances from relatively large particles can lead to the stabilisation of suspensions and emulsions for optimum electrolyte concentrations and a_1/a_2 ratios. Many experimental data confirming this conclusion are available. But it has been observed that small particles in rubber latexes execute "irregular" motions around large globules, behaving, as it were, as satellites of the latter[281,282]. Bethold and Snyder[278] patented a method for increasing the size of silica particles and for obtaining a stable sol containing 30 vol.% of the disperse phase by mixing suspensions with different degrees of dispersion.

Examination of the interaction of ellipsoids of rotation[215] showed that, in the presence of a repulsion barrier and a deep secondary minimum, the fixation of particles takes place preferentially for a parallel orientation of the symmetry axes (Fig. 7*a*). Since the size of the barrier is to a first approximation proportional to the radius of curvature[75], the probability of aggregation of greatly extended ellipsoids via their vertices is high for a particular ratio of the attraction and repulsion forces and there is a possibility of aggregation over both short and long distances (Fig. 7*b*). The fixation of anisodiametric particles when anisotropic forces (for example, dipolar forces) operate between them should occur with a relative shift of the particles, i.e. for angles in the range $0 \leq \gamma < \pi/2$, where γ is the angle between the direction of the principal symmetry axis of the ellipsoids and the line joining their centres (Fig. 7*c*).

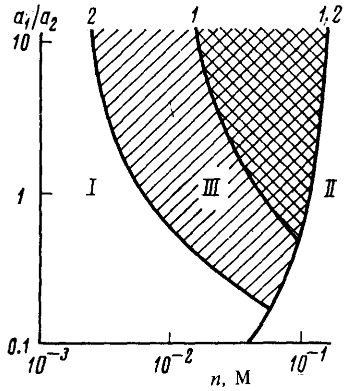

Figure 6. Stability diagrams of disperse systems consisting of particles of different sizes (a_2 = 0.1 μm) with (curve *1*) and without (curve *2*) allowance for the electromagnetic retardation effect: I) the region of the existence of stable systems; II) the region of short-range coagulation; III) the region of long-range coagulation.

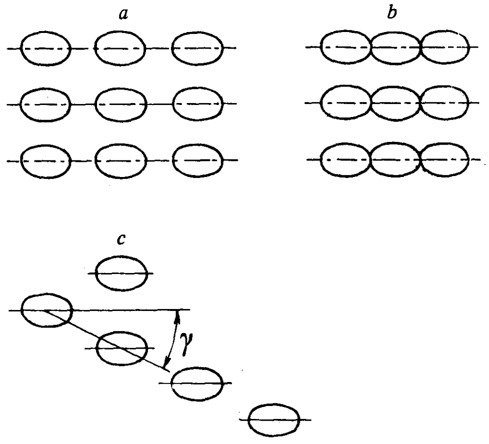

Figure 7. A scheme characterising the distribution of ellipsoidal particles and the formation of periodic colloid structures.

The structures arising as a result of the interaction of non-spherical (or spherical but non-polarised) particles usually possess anisotropic properties. Here one should mention in the first place a wide variety of periodic tactoid structures consisting of particles in the form of plates and rods[67]. Chain aggregates or dendritic structures arise as a result of dipole–dipole interaction from spherical monodisperse systems of particles placed in an electric field (Fig. 4). Similar behaviour has been observed for many tactoids also in the absence of an external field (Fig. 8).

Figure 8. A scheme characterising the distribution of particles in tactoids.

Tactoids are the simplest (model) periodic colloid structures of the local type, the formation of which is determined by the fixation of the particles at a secondary minimum and is accompanied by the loss of potential energy ($\Delta U < 0$).[5-7,13,22,23] They are closely related, on the one hand, to liquid crystals and liquid-crystal phases in solutions of soaps, lipoids, and polymers† and, on the other hand, to gels, pastes, and gel-like systems. The similarity of the structures of local type, i.e. structures which usually do not arise throughout the volume of the dispersion‡, has been noted for a long time by many investigators[15-17,283,284].

IV. THE INTERACTION OF PARTICLES UNDER "CONSTRAINED" CONDITIONS AND THE FORMATION OF PERIODIC COLLOID STRUCTURES WITH A LIMITED VOLUME OF THE MEDIUM

In stable colloid systems "constrained" conditions arise as a result of the increase of the concentration of the disperse phase. The increase of the number of particles involved in free Brownian motion prior to this leads to their mutual approach and to the overlapping of the ionic atmosphere or solvation shells and hence to the appearance of repulsion forces. In this case the average distance between the interacting surfaces becomes smaller than the coordinate H_0 corresponding to the secondary minimum on the pair potential curve (Fig. 9). A further increase of the concentration of the particles decreases the stability of the system in consequence of the decrease of the depth of the potential wells located in the region of positive values of the energy[45,46,285].

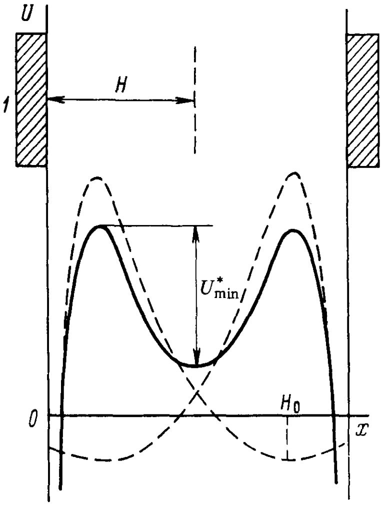

Figure 9. Dependence of the energy of interaction of particles *1* and *2* with a third particle on distance under restricted volume conditions. The dashed curves characterise the pair interaction potential.

For periodic colloid structures in a limited volume of the medium, an increase of potential energy is a characteristic feature ($\Delta U > 0$); they are formed throughout the volume of the system. The latter factor is responsible for the large-scale order in the distribution of the colloid particles, which can be readily observed from the bright iridescent colour of the dispersion[4,10,11,286]. In this case the periodic colloid structures play the role of a diffraction grating; the appearance of iridescence shows that the distances between the particles (and the dimensions of the particles themselves) are comparable to the wavelength of the transmitted light.

Numerous periodic colloid structures of the second type have been ovserved in latexes[4-8,10,11,210,286-291]. Many investigators have observed surprisingly regular lattices of latex particles (Figs. 1 and 2). In the stage preceding the formation of such quasicrystalline two-dimensional periodic colloid structures, the dispersion consisted of stable particles between which repulsion forces with a fairly large radius of action operated. "Constrained" conditions arose in such cases usually as a result of the evaporation of the liquid medium. In the Schiller layers, in deposits consisting of particles resistant to mutual aggregation, and also in creamy compositions, the restriction of the volume and "constrained" conditions are usually caused by gravitational or centrifugal forces.

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†A comparative study of colloid particles and associated complexes of dissolved polyelectrolyte macromolecules has led to the conclusion that the interaction of these particles [as well as the interaction of the swelling latex particles (micelles) in surfactant solutions] is determined by general relations, which may be determined on the basis of unique physical principles.

‡ Under certain conditions and for a sufficiently high concentration of the disperse phase, a complete immobilisation of the system is possible.

Thus repulsion forces are responsible for the appearance of periodic colloid structures of the second type and attraction forces give rise to local periodic colloid structures.

The Influence of Electrolytes on the Interaction of Particles under "Constrained Conditions"

It has been shown[210,287] that, depending on a number of parameters, aqueous dispersions of polyacrylonitrile can exist both in the form of mobile suspensions and in the gel-like state. At a low electrolyte concentration and in the presence of a fairly high content of the disperse phase, periodic colloid structures are formed in which the particles are separated by quasiequilibrium liquid layers as a result of strong ionic-electrostatic interactions. Such systems possess viscoelastic and viscoplastic properties. With increase of the concentration of electrolytes, the radius of action of the ionic-electrostatic repulsion forces diminishes, which either gives rise to structures made up of locally ordered regions or causes a conversion of the gel into a mobile fluid state characterised by the absence of shear strength. In the former case the regularity of the structure is maintained in consequence of the fixation of the particles at distances corresponding to the coordinate of the second minimum. One should note that the "liquefying" action of small amounts of salts has been observed previously by Fryling[288] and also by Brodnyan and Lloyd Kelley[289,290] in studies of the rheological behaviour of a number of latexes.

Table 4. The exponents ν for polyacrylonitrile dispersions in the presence of different concentrations of electrolytes (τ_0 is the limiting shear stress).

τ_0, dyn cm^{-2}	10^2[NaCl], M	10^4[MgCl$_2$], M	ν	τ_0, dyn cm^{-2}	10^2[NaCl], M	10^4[MgCl$_2$], M	ν
10	0.2	4.10	2.6	75	1.00	8.40	3.6
20	0.3	4.90	2.8	100	1.50	10.0	3.8
25	0.4	5.40	2.9	200	5.30	19.0	4.8
50	0.6	7.50	3.0	τ_{max}	16.0	26.0	6.0

The transition from long-range to short-range aggregation (coagulation) with increase of the concentration of electrolyte in the dispersion medium takes place gradually and frequently these stages of the structure formation process cannot be very clearly distinguished§. For example, the exponent ν in the equation nz^{ν} = const. for polyacrylonitrile dispersions in the concentration ranges 2.50×10^{-3}–1.00×10^{-2} M NaCl and 4.10×10^{-4}–8.40×10^{-4} M MgCl$_2$ amounts to 2.5–3.5, which demonstrates, according to Serebrovskaya and coworkers[201,202], the aggregation of particles with retention of the liquid layer separating them (Table 4).

The significant intensification of short-range aggregation at electrolyte concentrations close to the critical concentration n_c (5.30×10^{-2} M for NaCl and 1.90×10^{-3} M for MgCl$_2$) is responsible for the breakdown of the gel. The exponent $\nu = 6.0$ corresponds to this transition from the gel-like structure to a coagel, analogous to syneresis and accompanied by the evolution (displacement) of the syneretic liquid, which is consistent with the theory of the stability of lyophobic colloids[148-152], which has been used to prove the Schultze–Hardy rule in the form of Eqn. (19).

V. THE REVERSIBILITY OF PROCESSES INVOLVING THE FORMATION OF PERIODIC COLLOID STRUCTURES. PEPTISATION, THIXOTROPY, AND SYNERESIS

The mobility of the bonds between the elements of the quasicrystalline lattice, which is due to the comparatively small depth of the potential minimum, determines the most important properties of periodic colloid structures—the reversibility of the processes involving their formation and the possibility of peptisation and of thixotropic transformations.

A quantitative theory of these processes has not yet been devised. In discussing them, one must take into account the depths of the primary and secondary minima and also the changes in the conditions governing the mobile equilibrium (quasiequilibrium) between the particles fixed at the minima and existing in a free state in the bulk of the system. Indeed, experiment has shown that sol-gel transformations, induced by various physicochemical factors, can be regarded with some approximation as corresponding to equilibrium, as is assumed for crystallisation and dissolution processes. Naturally, this approach is justified only when coagulation and subsequent recrystallisation in the periodic colloid structures are very slow and do not have an appreciable influence on the aggregation equilibrium.

The existence of a mobile aggregation equilibrium in the aggregation of many colloid solutions has been observed by a number of investigators[5,22,23,52,53,209,242,253-255,292-299]. Thus, using an optical microscope, Okamoto and Hachisu[23] observed the Brownian movement of gold sol particles (forming aggregates) in the dispersion medium over a certain range of electrolyte concentrations. Using the method of the low-angle scattering of X-rays, Kratky et al.[299] measured the degree of aggregation of molecules in solutions of an azo-dye (Chlorantine Light Violet 2RLL) and established that the aggregation equilibrium depends on the concentration of the ions in solution, temperature, and the content of the dye. Similar relations were noted also in a study[297] of the coagulation of gold sols in a flow ultramicroscope.

In discussing the problem of the aggregation equilibrium in colloid solutions, Frens and Overbeek[294,295] concluded that the relation between the number of primary particles, the number of aggregates, and their size is determined by the minimum in the free energy of the system; for ion-stabilised dispersions, this minimum is related to the DL parameters. Thus there is a possibility in the DLVO theory of taking into account not only the processes involving the formation of aggregates but also their decomposition processes, determined by the finite depths of the primary and secondary minima.

Similar but more detailed ideas were developed in a series of studies by Martynov and Muller[300-303] for long-range aggregation or, in the authors' terminology,

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§ The transition from long-range to short-range aggregation may be observed from the disappearance of iridescence[286,291].

"barrierless coagulation"¶. It was shown that, under certain conditions, coagulation (aggregation) can occur only in consequence of a remote potential well[302]. Since the depth of this well is as a rule small, there is a comparatively high probability of the decomposition of the aggregate formed. One should note that the coagulation mechanism proposed by the authors[300–303] remains valid, subject to certain assumptions, also for systems a characteristic feature of which is the presence of a repulsion barrier between the particles: the relations established should hold also for a near potential well at electrolyte concentrations exceeding the critical value.

Analysis of the kinetics of slow coagulation[302], presupposing allowance for the decomposition processes of the aggregates formed, is of significant interest, since it has been found that the shape of the curves relating the total number of particles to time makes it possible to determine the decomposition coefficient and the depth of the potential well in which the fixation of the particles takes place. Furthermore, the height of the barrier can be found from the coefficient of the retardation of aggregation, and hence the fundamental parameters of the interaction between the particles may be calculated.

The decomposition of the aggregates and their formation take place spontaneously as quasiequilibrium processes; in contrast to this, peptisation and thixotropic transformations take place as a result of physicochemical and mechanical influences on the system.

Local Periodic Colloid Structures ($\Delta U < 0$)

Such structures, arising as a result of long-range aggregation, usually undergo peptisation comparatively readily; for example they consist of tactoids[18,19,22,23,241,253–255,283,304,305], freshly prepared gels and gel-like deposits[5,15–17,64,206–209,242,253–255,292–297], and flocculated emulsions[203,285,306–308]. Many disperse structures are peptised on simple contact with the dispersion medium containing stabilising ions or surfactant molecules, which occurs fairly frequently in the swelling of various argillaceous minerals[309–312] as well as pastes obtained from latexes, dyes, pigments[5], and colloid silver deposits[313].

However, one should bear in mind that peptisation is not usually quite complete (i.e. some of the precipitate remains)†. Thus the aggregation equilibrium in an AgI sol, observed on varying the concentration of the solid phase, changes with time: the aggregates are gradually stabilised and decompose to a lesser extent following dilution[313]. It is important to note that peptisation proceeds most completely when the electrolyte concentration in the intermicellar liquid in the initial state does not exceed the critical concentration causing the disappearance of the repulsion barrier[22,23,52,53].

Periodic Colloid Structures with a Limited Volume of the Medium ($\Delta U > 0$)

Such structures are characterised by their capacity for almost complete peptisation, since, following the decrease of the content of the disperse phase (the numerical concentration), the system tends to pass to a lower energy level, which is accompanied by a simultaneous increase of entropy‡. This process has been studied experimentally[10,52,53,210,291].

Anomalous Liquid Layers

Anomalous liquid layers preventing direct contact between the particles play an important role in peptisation processes, like the adsorption of ions from solution at the interface, which alters significantly the ion-electrostatic interaction of the particles. The influence of these factors on peptisation can be followed in relation to the intracrystalline swelling of various argillaceous minerals in electrolyte solutions. Norrish[309] showed by the method of low-angle X-ray scattering that the interplanar spacings H_B in swollen montmorillonite are to a large extent determined by the position of the exchangeable cation in the lyotropic series and its concentration in solution. For H^+ and Li^+ ions, H_B varies linearly to a first approximation as a function of $1/\sqrt{n}$; Na-montmorillonite exhibits the same relation at electrolyte concentrations $n < 0.3$ M, while at a concentration of approximately 0.3 M the interplanar spacings can be simultaneously $H_B = 19$ and 40 Å.

The interplanar spacings in specimens of an argillaceous mineral placed in KCl, NH_4Cl, and CsCl solutions do not as a rule exceed 15 Å whatever the concentration of the electrolyte. However, it has been observed[309,317] that the capacity of K-montmorillonite specimens for swelling depends on the method of their preparation. K-Montmorillonite which had been kept in a concentrated KCl solution and then placed in a dilute KCl solution does not swell, in contrast to the Li- and Na-montmorillonites in LiCl and NaCl solutions. At the same time, when a clay specimen which had been subjected to preliminary treatment in a dilute NaCl solution is placed in a dilute KCl solution, the high values $H_B \simeq 100$ Å persist after the exchange of Na^+ ions for K^+ ions and the lattice does not undergo appreciable changes.

The experimentally observed intracrystalline swelling of various cationic forms of montmorillonite has been explained[318] on the basis of the theory of the interaction of dispersed particles and the values of H_B have been calculated as a function of the concentration of the electrolyte in the disperse medium and have been found to agree fairly well with the experimental data, qualitatively and quantitatively. It proved necessary to take into account the specific adsorption of the ions in the dense component of the DL as well as the limit of the plastic strength of water near the interface[319–321].

The shear strength of the liquid layers should lead to the appearance of hysteresis loops in swelling–contraction processes[320–323]. For example, when the concentration

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¶ We believe that the term "barrierless coagulation" cannot be regarded as successful, since it corresponds merely to the model adopted by the authors in which infinitely large barriers and hence the absence of coagulation at the primary minimum are postulated.

† The periodic colloid structures corresponding to thermodynamic equilibrium as well as those in which the particles are separated by very high repulsion barriers, which brings the system closer to equilibrium, are apparently exceptions.

‡ The conditions governing the formation and existence of spontaneously dispersable systems with low interfacial energies have been discussed[314–316].

of the electrolyte is varied, the volume of the sedimentation deposit of Oglanlinsk Na-bentonite varies as in intracrystalline swelling[322], but the branches of the curve corresponding to the decrease and increase of the concentration of ions in the dispersion medium do not coincide. This type of variation must be explained by the fact that, on swelling, the shear strength of the liquid prevents the mutual separation of the elementary packets of montmorillonite and on contraction it prevents their mutual approach.

The problem of the capacity for peptisation of local periodic colloid structures is closely related to the phenomenon of thixotropy, i.e. to the ability of the structure to be restored after its disturbance under the influence of mechanical stress (stirring, vibration, etc.). Such a transition is usually accompanied by a change of effective viscosity by several orders of magnitude. At the same time it is known that, together with ideal thixotropy, there are many instances of an incomplete restoration of the strength characteristics of periodic colloid structures: in each succeeding thixotropic transformation, the volume occupied by the gel diminishes to an increasing extent until the disperse phase separates in the form of a dense deposit. Under these conditions, the strength of the gel frequently increases and the restoration period shortens. However, in many systems there is a characteristic decrease of strength and a gradual liquefaction of the gel, leading to complete irreversibility. Many gels (as a rule dilute gels) have no thixotropic properties: their strength is not restored even after the first disruption of the structure. Thus there are intermediate types between ideal thixotropic systems and systems without thixotropic properties[5].

Various processes resulting in a decrease of the strength of colloid structures, i.e. in liquefaction, are frequently classified as thixotropic. However, liquefaction can also occur as a result of slow coagulation, which disrupts the gel lattice and causes a sharp decrease in strength. The latter evidently has no bearing on thixotropy and is more likely to be a syneretic process. In particular, this is frequently observed in periodic colloid structures with a limited volume of the medium: coagulation (fixation at the primary minimum) leads to an increase of the distances between the particles or their aggregates, which is responsible for the disruption of the lattice of the gel and hence for the decrease in its strength.

The processes occurring in syneresis may be examined on the basis of the theory of slow coagulation, where, however, one must take into account the cooperative effect, i.e. the influence of a single particle attached to the aggregate on the interaction of all the particles. This constitutes a very difficult task. The current theory of slow coagulation[197-199] is based on the concept of pair interaction between particles, which has been justified with adequate approximation for dilute systems. In gels, each particle is surrounded by neighbours and the energy of their collective interaction must be expressed by the exponent in Eqn. (20). The overall height of the barrier $U^*_{\max}$ for the pair interaction is defined, according to Wiese and Healy[65], as the arithmetical sum of the absolute height of the repulsion barrier $U_{\max}$ and the depth of the secondary minimum $U_{\min}$.

Phenomena analogous to thixotropic recovery processes frequently occur in disperse systems under the influence of external force fields: electrical, magnetic, ultrasonic, etc. In dilute dispersions, these fields are responsible for the formation of structures, for example chain aggregates, which may decompose after the removal of the field, i.e. may be spontaneously peptised[121,124,125,128,324].

VI. ESTIMATION OF THE INTERACTION FORCES BETWEEN DISPERSED PARTICLES ON THE BASIS OF THE RHEOLOGICAL PROPERTIES OF PERIODIC COLLOID STRUCTURES

When specific deformation processes in colloidal dispersions, pastes, and deposits are considered, it is important to know the relation between the stresses operating in the system and its flow rate. Problems of this kind constitute the subject of rheology—the science of the fluidity of matter[325]. However, rheology, which is a component of physochemical mechanics[25,26], is restricted to phenomenological methods for the description of the deformation process without elucidating the relation between the strength of disperse systems and the surface forces of the interaction between particles. Furthermore, the latter problem, the solution of which is apparently still in its initial stage, is of great practical importance, primarily for the development of new methods whereby various materials with specified properties could be obtained[326].

Periodic colloid structures usually have a high yield point and they can therefore be regarded as plastic solids or, according to Rebinder's classification[14,327], as solid systems, in contrast to liquid systems (dilute sols, emulsions, etc.) for which the yield point is zero. The calculation of the strength of such systems is as a rule based on model concepts and certain assumptions concerning the parameters of the interaction of the particles. The models employed evidently constitute only a first approximation and do not fully reflect the real structure of the disperse material. This applies mainly to systems characterised by low equilibrium (quasiequilibrium) distances between individual particles and hence a significant non-uniformity of the distribution of particles in the bulk phase of disperse porous bodies. For periodic colloid structures of the local type and particularly for such structures formed under the conditions of a restricted volume, the introduction of model concepts is fully justified, although the methods of calculation in the case of short-range and long-range aggregation are not fundamentally different.

In most studies dealing with the strength of gels and gel-like systems, a uniform distribution of the particles of the disperse phase is postulated. For example, in a study of glyceryl tristearite suspensions in hydrocarbons, Nederveen[328] determined the average distance between the particles, assuming that van der Waals–London forces as well as Born repulsion forces operate between them, and calculated the moduli of elasticity of the dispersions from the formula proposed by van den Tempe[329]. The appreciable discrepancies between the experimental and calculated data were accounted for by the imperfection of the model.

Volarovich and Gutkin[330] showed that the limiting stresses due to the existence of periodic colloid structures, occurring in simple shear deformation, may be found from the expression

$$\tau_0 = \frac{4}{\pi} N U_0, \qquad (23)$$

where U_0 is the energy of the pair interaction of the particles. On the assumption that the fixation of the particles in the lattice takes place owing to long-range dipolar forces, the authors[331] calculated the values of τ_0, which were in the order of hundreds of dyn cm^{-2} and were close to the values of τ_0 observed experimentally for a number of suspensions[332].

A similar model was also used in another study[8], where the relation between the limiting shear stresses in periodic colloid structures was considered as a function of the concentration of the solid phase and of the electrolyte in the dispersion medium. Molecular and ionic-electrostatic interaction forces between the particles were taken into account, while the energy of the interaction of rigid electrical dipoles, which should probably be shielded by the counterdipoles in electrolyte solutions, were disregarded. The results of the calculations, which are in good qualitative and quantitative agreement with experimental data, explained many of the known facts, namely the decrease of the strength of periodic colloid structures of the second type with increase of the concentration of ions in the system[210], the parabolic relation between τ_0 and the numerical concentration of the particles[287], etc.

A chain model of disperse structures has been proposed by Rebinder et al.[326] It is designed mainly for the calculation of the strength of disperse materials such as catalysts, the porosity of which may vary within wide limits, although it can be used successfully also for estimating the mechanical properties of local periodic colloid structures. In constructing the model, the occurrence of chain aggregates consisting of spherical particles of identical size in contact was postulated. The chains are distributed along three mutually perpendicular directions and intersect, forming nodal points. In order to characterise the system, it is sufficient to know the diameter of the particles $2a$ and their number N_0 in the aggregate; its strength Q_m depends on the strength q_1 of a single contact and

$$Q_m \simeq 10^{10} q_1 \frac{1}{d^2} \beta, \tag{24}$$

where d is the average pore diameter in angstroms, Q_m is expressed in kgf cm^{-2}, and $\beta = 4/\pi - 2/N_0 + 1/N_0^2$.

An experimental test of Eqn. (24), showed that the equation predicts fairly accurately the force of cohesion of the particles q_1, provided that Q_m is known[333]. At the same time, it has been stated[333] that the difference between the values of q_1, found from the results of microscopic and macroscopic measurements, may be attributed to some uncertainty in the estimation of q_1 from the measured strength of individual contacts, which varies within the limits of six orders of magnitude.

A somewhat modified model of disperse structures, consisting of a series of repetitions of the same unit cell (which is not necessarily closed), was proposed by Yakhnin and Taubman[334]. The basic element of the cell is a conventional edge containing N_0 particles having the same diameter $2a$. Then

$$Q_m = kq_1/a^2 N_0^2, \tag{25}$$

where k is a dimensionless coefficient, which depends on the shape of the cell and the fraction of the effective (structural) units in the chain. It is important to note that the concepts developed by the authors[334] have been extended to the case of the particles of the disperse phase modified by surface-active substances, which alter the forces of interaction between the particles. Subsequently the distribution of the particles with respect to cohesive forces was taken into account within the framework of the model of Yakhnin and Taubman[335].

Considering the dissipation of energy of the flow of a plastic material, Michaels and Bolger[336] showed that the limiting shear stresses may be calculated from the equation

$$\tau_0 = \frac{3\varphi}{2\pi^2 a^3} U_0, \tag{26}$$

where φ is the bulk-phase concentration of the solid. The derivation of Eqn. (26) is not associated with model concepts, is general, and does not involve any assumptions concerning the nature of the linkages between the particles. Using this approach, Hunter and coworkers[337-339] subsequently investigated the problem of the influence of electrical double layers, temperature, and steric stabilisation of suspensions on the energy of cohesion of the particles in the aggregate U_0.

Information about the interaction of the particles can be obtained from compression measurements[340, 341] and also from data obtained by studying the elastic properties of dispersions[342]. For example, Ottewill and coworkers[340] found the interaction forces between the particles as a function of the distance H between their surfaces by determining the dependence of the elastic deformation of moisture-saturated Na-montmorillonite specimens and powders containing monodisperse polystyrene particles on the external load. The electron-microscope photographs of the latex quoted by the authors[340] permit the conclusion that the distribution of particles in the systems investigated is fairly rigorously ordered, and the systems can probably be classified as periodic colloid structures with a limited volume of the medium, since the range of variation of H for all loads amounted to several tens and hundreds of angstroms.

The application of external electrical and magnetic fields and the associated electrorheological[124-132] and magnetorheological[226, 343] aggregation effects proved to be extremely promising for the estimation of the degree of interaction between dispersed particles. In contrast to spontaneously coagulated suspensions and sols, the aggregates arising under the influence of the fields are extended, which significantly facilitates the interpretation of experimental data. In consequence of the rapid development of a number of fields in chemical engineering, where electrical and magnetic treatment of disperse systems is being used on an increasing scale, such studies assume particular urgency.

The theoretical and experimental data concerning the long-range interaction of colloid particles confirm the validity of ideas about periodic colloid structures of the first and second types. In order to devise a rigorous theory of the processes involved in the formation of such systems, which is very important for the successful development of the science of surface phenomena and for the improvement of various technological processes, it is necessary to solve many complex problems, which arise primarily in consequence of the insufficiently complete investigation of the interaction forces between particles. Thus there are no methods for the calculation of the forces acting between surfaces having anomalous liquid layers or between surfaces separated by a layer or solution with a high concentration of ions; the theory of the interaction of surfaces stabilised by surfactants and polymers has been inadequately developed, and so on. Particular mention should be made of the necessity for the solution of the problem of the collective interaction of particles, which can occur in general under the influence of attraction and repulsion forces of different types.

Latexes containing virtually monodispersed spherical particles have been used recently with increasing frequency as model systems for the investigation of structure formation processes. The results for the study of such dispersions have been widely discussed in the present review. However, this does not mean that latexes occupy a dominant position among other periodic colloid structures, which are common in nature and industry, although their importance is many respects incontrovertible. There is no doubt that certain sedimentary rocks, soils, cement pastes, ceramic and paper compositions, clay dispersions, gelled emulsions and foams, creams, etc. are of primary importance. Unfortunately their extensive investigation is complicated by the fact that they are usually polydisperse, the shape of the particles is irregular, many components, including various impurities, are present, and frequently also both chemical and physicochemical processes take place. It therefore appears to be necessary to investigate systematically and thoroughly real polydisperse systems for variable values of different parameters, which will help in the solution of theoretical and practical problems. The research must be directed primarily towards the study of the influence of electrolytes, temperature, and other factors on long-range aggregation, peptisation, thixotropic transformations, and syneresis, as well as the rheological properties of periodic colloid structures.

The determination of the relations governing the behaviour of particles in dispersions is possible on the basis of the theory of molecular and ionic solutions, the development and improvement of which constitutes a very complex and topical problem at the present time.

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Nucleophilic Substitution of Hydrogen in Aromatic Systems

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The literature data on the substitution of hydrogen under the influence of nucleophilic agents in aromatic and heteroaromatic systems and in quinones are reviewed. The absence of anionic stabilisation of the hydrogen substituted with its pair of binding electrons is responsible for the specific nature of the reactions under consideration, which is different from that of the nucleophilic substitution of other species and from that of the electrophilic substitution of hydrogen, necessitating the use of an oxidant in most instances.
The bibliography includes 227 references.

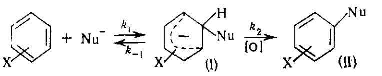
CONTENTS

I. INTRODUCTION

In one form or another the problems of the nucleophilic substitution of hydrogen have been reflected in the literature on nucleophilic aromatic substitution of anionically stabilised groups [1,2] and hydride shifts [3-5], in reviews dealing with aromatic and heteroatomic cations [6-9]. There exists a monograph [10] as well as a series of review articles on the nucleophilic aromatic [11-17] and heteroaromatic [18-21] substitution of anionic bearing groups. Concepts concerning the structures of the intermediate σ complexes [15-17], the involvement of π complexes [21], and the role of one-electron steps in such reactions [22-27] have been developed with the aid of chemical and physical methods. Extensive data have been accumulated, including quantitative measurements of kinetic and thermodynamic parameters, correlations between the rate constants and the influence of the activating or eliminated group, and solvation, catalytic, and isotopic effects. However, these results can by no means always be used to interpret the nucleophilic substitution of aromatically combined hydrogen, because such reactions are different from the electrophilic substitution of hydrogen as well as from the nucleophilic substitution of anionically stabilised species†.

The hydride ion is not involved in the formation of hydrogen bonds, is not solvated, and shows no tendency whatever towards any anionic stabilisation. Anionic or anionoid σ complexes, containing hydrogen at the germinal site, are as a rule more stable than the corresponding structures with a group capable of being stabilised in the form of an anion. For this reason it has come to be accepted [28] that the removal of the hydride ion involves considerable difficulties and requires several conditions. This is probably the case when the hydride ion is removed as such without using an oxidant. A dehydrogenating oxidising agent may be deliberately introduced into the reaction mixture or, for a favourable ratio of the oxidation-reduction potentials of the σ complexes and the starting materials, the substrate itself can serve as the oxidant. In the present review it is shown that the use of an oxidant can lead to low activation energies and to the possibility of carrying out the process under mild conditions.

S_NH reactions probably proceed via a two-stage mechanism in the vast majority of cases with formation of an intermediate. The mechanism shows that, depending on the ratio of the rate constants, the interaction can proceed in different ways:



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The constant k_2 depends on the ratio of the oxidation-reduction potentials of the intermediate (I) and the oxidant. When $k_1 \gg k_{-1}$ and k_2 is large, the process is completed with formation of the product (II). When $k_1 \gg k_{-1}$ and k_2 is small, the reaction may stop at the stage of the product (I); when $k_1 \ll k_{-1}$ and k_2 is large, the σ complex (I) is present at a vanishingly low quasistationary concentration and the process can develop only in the presence of an appropriately selected oxidant. In the absence of an oxidant or when its oxidising capacity is inadequate, other processes may be observed—the substitution of other groups when these are present or the dimerisation of the substrate.

The fact that in many instances σ complexes can be isolated in a pure state in S_NH reactions is in all probability responsible for the lack of terminological consistency in the description of such reactions: they are sometimes regarded as addition reactions even in those instances where the intermediate has not been isolated and has not been detected by other methods [29,30]. According to Ingold, the term "bimolecular nucleophilic substitution" can be applied to all such reactions, despite the existence of intermediate addition products [28].

In the present review an attempt has been made to treat from general standpoints the S_NH reactions in various aromatic systems, both activated and not activated by nitro- and aza-groups, and in quinones. Such parallels can be usefully drawn in the treatment of nucleophilic substitution of hydrogen and related phenomena. Particular attention has been devoted to the elucidation of the role of the oxidant in these processes and also to the discussion of the quantitative data characterising the reactions of the S_NH type in the series of aromatic compounds.

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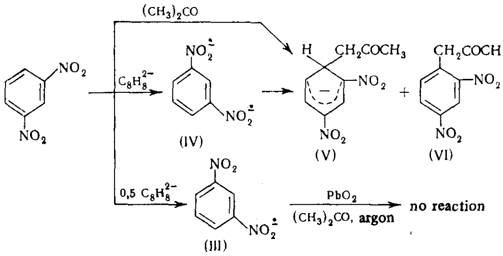
†We suggest that nucleophilic substitution of hydrogen be designated by the symbol S_NH, emphasising the specific nature of such reactions.

II. S_NH REACTIONS OF NITRO-COMPOUNDS

The reactions of aromatic compounds activated by a nitro-group with different nucleophiles have all the features of the interaction between an electron donor and acceptor (oxidant and reductant) and depend on the number and positions of the nitro-groups in the substrate, the nature of the nucleophile, and the involvement of the oxidant. The interaction can result in the respective formation of donor–acceptor complexes, anionic σ complexes (Meisenheimer complexes), or products of the nucleophilic substitution of hydrogen. An increasing amount of data is being published, showing that the products obtained as a result of complete electron transfer can play a significant role also in S_NH reactions[23].

As an example, one may quote a study of the reaction of *m*-dinitrobenzene with the carbanion formed from acetone in an alkaline medium (Yanovskii's reaction). Gol'teuzen et al.[31] resorted to the simulation of electron transfer processes using the cyclooctatetraene dianion $C_8H_8^{2-}$ instead of the acetone carbanion:



By adding specific amounts of this dianion, it was possible to control separately the formation of both the radical-anion (III) and the biradical-dianion (IV) from dinitrobenzene. It was established that the radical-anion (III) is not involved in the reaction with the acetone anion, while the dianion (IV) yields the product of Yanovskii's reaction—the σ complex (V), together with the product (VI) of the nucleophilic substitution of hydrogen. This provides a sound basis for the assumption that the biradical-dianion (IV) is located on the reaction coordinate in the formation of the σ complex (V). Other examples indicating that the involvement of electron transfer products in reactions of the S_NH type is quite likely are also known[27,32].

Whether or not the reaction stops at the Meisenheimer addition stage depends to a considerable degree on how effectively the negative charge is delocalised over the electron-accepting groups. The differences between the delocalisation energies on passing from aromatic nitro-compounds to anionic σ complexes (−8 kcal mole^{-1} for nitrobenzene, 1 kcal mole^{-1} for 2,4-dinitrobenzene, and 10 kcal mole^{-1} for 1,3,5-trinitrobenzene) show how strong is the influence of the successive introduction of nitro-groups in the *meta*-positions[33].

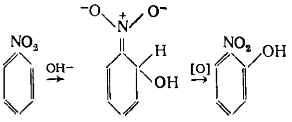
Numerous stable Meisenheimer complexes containing a hydrogen atom at the geminal site have been described[15]. Their oxidation makes it possible to obtain substituted aromatic polynitro-compounds, although in the literature there are only isolated reports on this problem[34-36]. Studies indicating a systematic approach to the investigation of the oxidation of hydride-active hydrogen in anionic σ complexes were only published as late as 1973–1974.[37,38] It has been shown[37] that both two-electron (the tropylium cation, lead tetraacetate, hypohalogenites, and halogens) and one-electron [Fenton's reagent, silver nitrate, and iron(III) chloride] oxidants can be used for the oxidation reaction and that the rate of oxidation depends on the standard potential of the oxidant. The first quantitative data appear to have been obtained[38] (Table 1) for the oxidation potentials of the anionic σ complexes at a rotating platinum electrode. They demonstrate the necessity for the use of a strong oxidant in order to obtain substituted polynitro-compounds.

Table 1. The polarographic oxidation potentials of the σ complexes of nitro-compounds with acetone in 0.1 *N* $(C_4H_9)_4NClO_4$ as the supporting electrolyte (relative to the saturated calomel electrode).

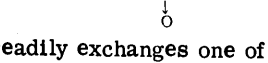
Initial nitro-compound	$E_{1/2}$, V	*E*, mV	No.of electrons	Reversibility
1,3-Dinitrobenzene	0.330	85	2	Irreversible
2,4-Dinitroanisole	0.325	75	2	»
1,3,5-Trinitrobenzene	0.825	80	2	»

The use of optimal conditions ensures a fairly smooth course of the S_NH reactions of nitro-compounds, which makes them important on a preparative scale and in some cases on an industrial scale. Examples of such reactions are considered below.

The treatment of nitrobenzene with dry powdered alkali has been known for a long time as a method for the synthesis of *o*-nitrophenol:[39,40]



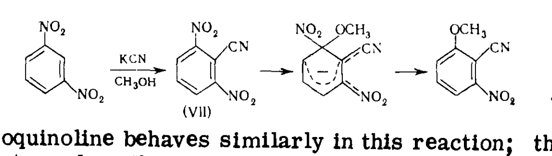
Presumably the residue eliminated here is a free hydride ion, which is accepted by the oxidant. The oxidant may be potassium nitrate or hexacyanoferrate(III). In the absence of an oxidant, nitrobenzene itself plays the role of the hydride ion acceptor, being reduced to azoxybenzene:



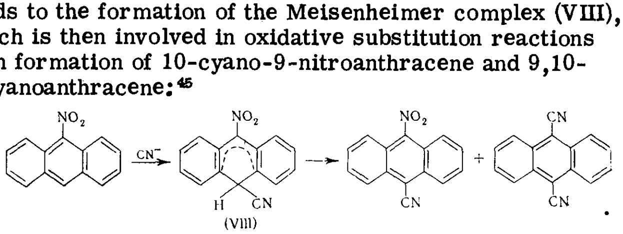
$$C_6H_5NO_2 \xrightarrow{H^-} C_6H_5{-}\underset{\underset{O}{\downarrow}}{N}{=}N{-}C_6H_5$$

Trinitrobenzene readily exchanges one of its hydrogens for a hydroxy-group, forming picric acid when it is acted upon by an alkaline solution of potassium hexacyanoferrate(III).[41]

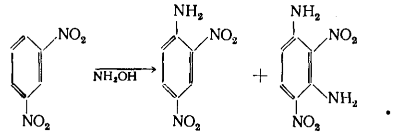
The cyanide ion is able to substitute hydrogen in the 2-position of *m*-dinitrobenzene[42]; the nitro-compound present in excess serves as the H^- acceptor. It is of interest that the reaction does not then stop. The dinitrobenzonitrile(VII) formed is so electrophilic that it captures an alkoxide anion, the steady-state concentration of which is undoubtedly very low. Under these conditions, one of the acceptors (the nitro-group) leaves the system:



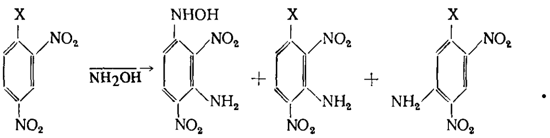
6-Nitroquinoline behaves similarly in this reaction; the heteroatom plays the role of a second nitro-group.[43] Picric acid forms a disubstitution product with KCN, the capture of hydride residues proceeding via an intramolecular mechanism and being completed by the formation of a hydroxylamine derivative[44]. The reaction of 9-nitroanthracene with the cyanide ion in dimethylformamide leads to the formation of the Meisenheimer complex (VIII), which is then involved in oxidative substitution reactions with formation of 10-cyano-9-nitroanthracene and 9,10-dicyanoanthracene:[45]


(VIII)

The reaction of dinitrobenzene with hydroxylamine in an alcoholic alkaline solution, discovered by Meisenheimer and Patzig[46], is an interesting example of the direct substitution of hydrogen by a nucleophile:

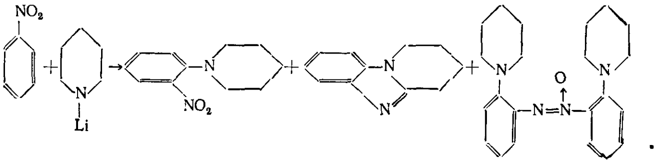


The reaction proceeds under mild conditions and with an almost quantitative yield, which makes it preparatively important. It was established that the introduction of a methyl group lowers the reactivity of dinitrobenzene, while the introduction of a nitro-group increases it. Subsequently Gitis et al.[47] established the mechanism of this reaction; they also made a more detailed study of the influence of the ring substituent on the reactivity of *m*-dinitrobenzene and identified three types of substitution products[48]:



On reaction with hydroxylamine, 2-nitronaphthalene forms 2-nitro-1-naphthylamine, while trinitrobenzene gives rise to picramide.[46]

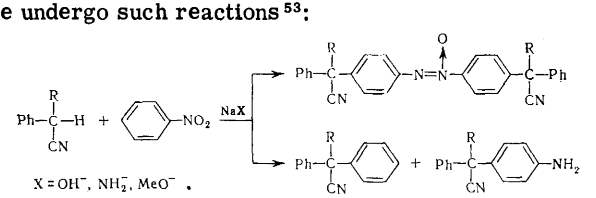
Alkyl and aryl derivatives of lithium and Grignard reagents reduce nitro-compounds. In contrast to this, organic amides give rise to the substitution of the hydride ion. Thus lithium piperidide reacts with nitrobenzene to form a low yield of the *ortho*-substitution product (IX) together with its ring-closure product [1,2-tetramethylenebenzimidazole (X)] and reduction product [2,2′-dipiperidinoazoxybenzene (XI)]:[49]


(IX) (X) (XI)

The sodium salts of amines form as a rule *para*-substitution products: on reaction with nitrobenzene, sodium piperidide yields 9-(*p*-nitrophenyl)piperidine[50], while the potassium salt of carbazole forms 9-(*p*-nitrophenyl)carbazole[51]. Sodium diphenylamide is involved in a similar reaction[52].

Contrary to expectation, on being mixed with sodamide in liquid ammonia, nitrobenzene is not involved in a Chichibabin substitution reaction, but forms a complex mixture of unidentified products[50].

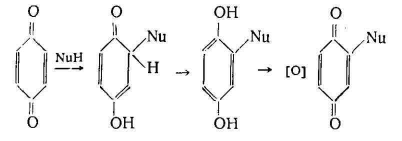
The carbanions formed from CH acids in the presence of bases give rise to Meisenheimer complexes on reaction with polynitro-compounds[15]. These are usually fairly stable products, but can be converted into substitution products by choosing an appropriate oxidant[37,38]. Comparatively recently, it proved possible to make nitrobenzene undergo such reactions[53]:



III. S_NH REACTIONS OF QUINONES

Quinones are not aromatic compounds; they can be classified as unsaturated cyclic $\alpha\beta$-diketones. However, although ketones do not in fact belong to the class of aromatic compounds, they are very close to them genetically and readily regenerate a benzenoid structure. Comparison of similar S_NH reactions of quinones and aromatic (and heteroaromatic) compounds permits a better understanding of the general nature of such processes. The reactions of quinones with nucleophiles are of interest as models of oxidation-reduction processes occurring in organisms with participation of *p*-benzoquinone and 1,4-naphthoquinone derivatives—ubiquinones and tocopherylquinones[54,55].

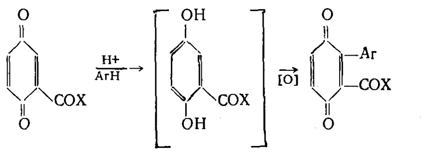
Quinones are involved in these processes as fairly active electrophiles—their interaction with uncharged nucleophiles involves the simultaneous nucleophilic substitution of hydrogen in the quinone and the electrophilic substitution of hydrogen in the nucleophile:


(XII)

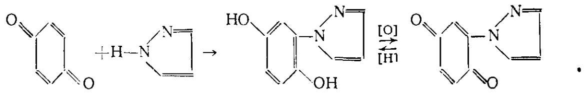
There is an initial 1,4-addition of the nucleophile to the quinone, completed by the formation of adducts having the structure of hydroquinones (XII). In order to convert them into substitution products, it is sometimes necessary to use an oxidant, although in certain instances intermediates of type (XII) have not been detected, the final substituted quinone being formed[29].

Reactions in which quinones form neither addition products nor hydrogen substitution products in the absence of an oxidant,[57] are discussed below.

It has been shown that benzoquinone and its carbonyl derivatives react under conditions of acid catalysis with nucleophiles such as dimethylaniline, phenols, or their ethers, and even alkylbenzenes.[58] With few exceptions, the reactions proceed at room temperature and are completed by the formation of arylbenzoquinones. Ag_2O is used for the oxidation of the adduct:


X=Me, OR .

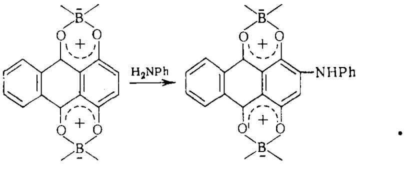
The interaction of quinones with heteroaromatic compounds having an excess of π electrons (pyrrole, furan, etc.) also leads to the formation of products of the substitution of hydrogen in quinones under oxidative conditions[59-61]. Pyrrole forms mono- and di-addition products involving the 2- and 5-positions or the 3-position, when the first two are occupied. Pyrazole reacts at the nitrogen atom and, as in the preceding case, the addition products are readily and reversibly oxidised[61]:



The interaction of benzo- and naptho-quinones with thiophen[62], furan[63,64], enol ethers[61], and CH acids[65] has also been investigated.

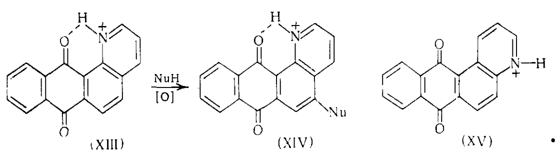
When reactions with diene-like nucleophiles (for example indole) are considered, one must bear in mind the possibility that quinones are involved not only in S_NH reactions but also in Diels–Alder addition reactions[29], which has not always been taken into account[66,67].

Direct nucleophilic attack on the quinone fragment is impossible in 9,10-anthraquinone, its activating effects being merely transmitted to the adjacent benzene ring. For this reason, anthraquinones are relatively inactive in the S_NH reactions characteristic of benzo- and naphthoquinones. For example, anthraquinone-2-sulphonic acid gives rise to alizarin only on being fused with alkali[68]. Anthraquinones containing in the *peri*-position with respect to the carbonyl group a substituent capable of combining with a proton and forming a chelate ring acquire greatly enhanced electrophilic properties and readily react with nucleophiles. Electronic interactions in chelate rings influence the distribution of electron density in the ring with the substituent, which is reflected in the localisation of the $C_{(2)}-C_{(3)}$ bond[69]. The influence of chelate formation on the reactivity is also manifested by the fact that 1-hydroxyanthraquinone is much more reactive in hydride-ion substitution reactions than 2-hydroxyanthraquinone. The involvement of boric acid as a catalyst in the arylamination of quinizarin[56] consists in the formation of a chelate ring, which increases sharply the reactivity of the substrate:



Direct amination with ammonia[70] and secondary amines[57] of 1- and 2-hydroxyanthraquinones and the substitution of hydrogen in the alkyl- and aryl-amine residues in quinizarin[71,72], 1-amino-4-hydroxyanthraquinone, and 1,4-diaminoanthraquinone[73] also belong to reactions of the type under consideration.

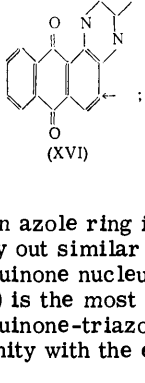
In a series of studies by Gorelik and coworkers, the influence of the heteroaromatic ring of the azine or azole type annelated to anthraquinone on the reactivity of the system with respect to a nucleophile was elucidated. The very important problem in the chemistry of anthraquinone discussed above, namely the increase of its electrophilic properties as a result of the involvement of the carbonyl group in chelate formation, is being solved by the synthesis of structures in which a favourable position of the protonated heterocyclic nitrogen permits the formation of a chelate ring with an intramolecular hydrogen bond. Under these conditions, two factors have a synergistic effect: the formation of the ammonium (azinium) cation and the enhancement of the electron-accepting properties of the carbonyl group. For example, the cation (XIII) reacts smoothly with thiophenoxides, sulphinic acids[74], and alkylamines[75], forming the substitution products (XIV):



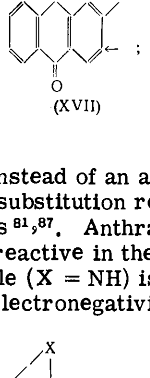
(XIII) (XIV) (XV)

The quinone (XV) does not enter into these reactions[74], which demonstrates the validity of the conclusion[69] that chelate formation plays an important role in the transfer of the positive charge in the chain and that there is conjugation in structures of type (XIII).

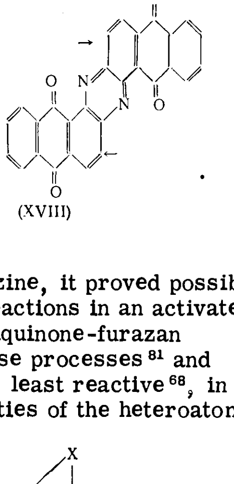
The activation of the anthraquinone nucleus by the annelation of an azine has been demonstrated for naphtho[2,3-*a*]phenazine-8,13-dione (XVI)[76-78], naphtho-[2,3]quinoxaline-7,12-diones (XVII)[79], and anthraquinone-azine (XVIII)[80][‡]:



(XVI)

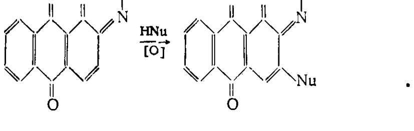


(XVII)



(XVIII)

Using an azole ring instead of an azine, it proved possible to carry out similar substitution reactions in an activated anthraquinone nucleus[81,87]. Anthraquinone-furazan (X = O) is the most reactive in these processes[81] and anthraquinone-triazole (X = NH) is least reactive[68], in conformity with the electronegativities of the heteroatoms:



Although in the majority of cases S_NH reactions take place in the anthraquinone nucleus, nevertheless nucleophilic attack involving also the annelated fragment has been described[78], in agreement with the results of quantum-chemical calculations[88].

The substitution of hydrogen atoms in anthrapyridone has been observed on treatment with amines[89], cyanide ions, and hydroxide ions[90]. The distribution of π-electron density and other reactivity indices of anthrapyridone are different[91] from those of the anthraquinones discussed

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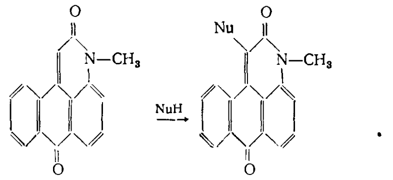
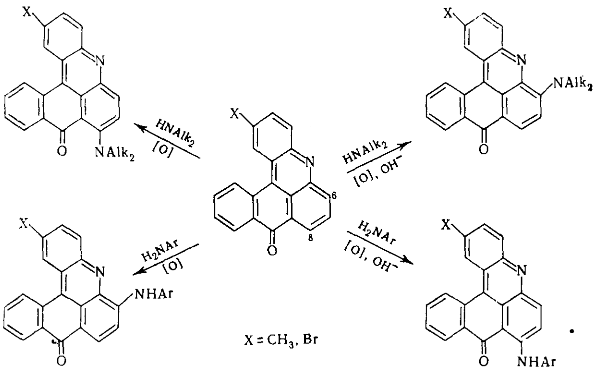
[‡] The arrows indicate the direction of nucleophilic attack.

above, since substitution takes place in the pyridine fragment. It is of interest that *N*-unsubstituted anthrapyridone does not react with amines, although this finding has not so far been explained:



The so-called ceramidonine—9*H*-naphtho[3,2,1-*kl*]-acridin-9-one–is an analogue of anthrapyridone. In contrast to anthrapyridone, in this case hydrogen is substituted in the anthraquinone part of the molecule[92,93]. The reaction is carried out in solution in pyridine under oxidising conditions, $KClO_3$ or $FeCl_3$ being used as oxidants.

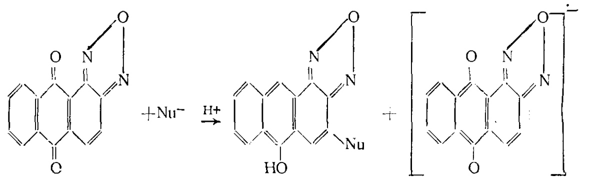
The direction of nucleophilic attack depends significantly on the nature of the amine and the presence of a base[92]. In the absence of bases, alkylamines substitute hydrogen in the 8-position and arylamines in the 6-position. The introduction of an alkali metal or tetraethylammonium hydroxide into the reaction mixture alters the orientation of the nucleophile and under these conditions an aromatic amine is directed to the 8-position and an aliphatic amine to the 6-position. A rare instance of the substitution of hydrogen rather than the halogen has been noted in the reaction of cyclohexylamine with 5-chloroanthraquinone-thiadiazole, in which the chlorine is activated with respect to nucleophilic substitution, according to current views, by both anthraquinone and thiadiazole components[94]:



A change in the direction of nucleophilic attack has also been observed in the amination of 1-hydroxyanthraquinone[72] by secondary alkyl amines. In aqueous solutions of dimethylamine and piperidine, the alkylamine residue substitutes hydrogen exclusively in the 2-position, while in pyridine solution substitution in the 2- and 4-positions takes place with formation of a mixture of products. In the absence of a solvent, 1-hydroxyanthraquinone gives rise to 1-hydroxy-2,4-dipiperidinoanthraquinone. The different modes of reaction have been explained by the characteristics of the solvation of both the initial amine and of the transition state arising when the 2- and 4-positions are attacked.

The role of the oxidant in the reactions of anthraquinone derivatives discussed above is exceptionally important. It determines the mode of reaction and the yield of products. In the oxidation of the unstable intermediate formed reversibly[95], the reaction is directed towards the nucleophilic substitution of hydrogen. In the absence of atmospheric oxygen or another oxidant, there is a possibility of several types of interaction of quinones with nucleophiles: (a) the reaction proceeds via the abstraction of a hydride ion from the intermediate by the initial quinone[82]; (b) the substitution reaction does not occur, the dimerisation of the substrate with formation of the corresponding bianthraquinonyl being observed[72,95]; (c) when the molecule contains a group capable of anionic stabilisation, it is substituted (for example, a hydroxy-group)[57].

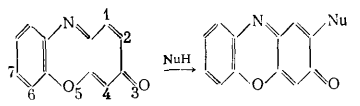
The interaction of anthraquinones with nucleophiles can occur during the initial period as a donor–acceptor process and instances of complete charge transfer have been noted. Thus radical-anions have been detected in the reactions of hydroxide ions with quinones[96] and of anthraquinones with sulphite ions[97,98], in the direct amination of quinizarin[57], and also in the nucleophilic substitution of hydrogen by CN^-, OH^-, and $OAlk^-$ ions in anthraquinone-furazan[84]:



(XIX) (XX)

Most of the initial quinone (XIX) is converted into the stable radical-anion (XX). It is believed that the formation of charge-transfer complex does not constitute an intermediate stage but proceeds as a parallel reaction[86]. On the other hand, it has been suggested that the radical-anions may precede the formation of σ complexes[97,98].

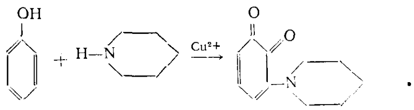
A series of studies have been made on the S_NH reactions of phenoxazinone derivatives[99–107]. In the fractions investigated, phenoxazinone, which contains the quinone imine fragment in its structure, exhibits much similarity with quinones:



Like quinones, phenoxazinones are capable of having their hydrogen substituted under oxidising conditions by residues of nucleophiles such as thiophenols[100], alkylamines[101], arylamines[102], arenesulphinic acids[103], and mercapto-compounds[104]. Hydrogen is apparently substituted always via a stage involving the formation of an intermediate addition product, which can be isolated when the experiment is carried out in the absence of air[105].

A systematic study has been made of the influence of the annelation of benzene rings on the electrophilic properties of phenoxazinone[106,107]. Analysis of the electronic structures of 2-phenoxazinone and its derivatives by the LCAO-MO method in the Hückel approximation showed[106] that benzophenoxazinones in which benzene is not annelated to the quinone imine component, contain, apart from the 7-position, a second electrophilic centre—the *peri*-position with respect to the heterocyclic nitrogen in the quinonoid ring. The calculated data were confirmed experimentally; a mixture of three compounds was found in the reactions of 3-phenoxazinone with thiophenols: 7-substituted, 1-substituted, and 1,7-disubstituted 3-phenoxazinone derivatives[107]. The method of oxidative amination of phenols discovered in 1955 by Brackman and

Havinga[108] has considerable synthetic possibilities. The above workers established that amino-*o*-quinones can be obtained by oxidising phenol and 2-naphthol with oxygen in the presence of the copper complex of morpholin.



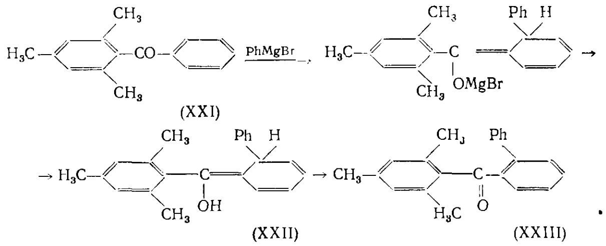
Phenol is initially oxidised to *o*-quinone, which then undergoes the S_NH reaction. Still earlier it was shown that catechol is involved in the oxidative amination reaction[109]. Sodium iodate in alcohol can also be used as the oxidant in this reaction[110].

Subsequently this method was successfully extended to phenols containing annelated azine[111–115] and azole[116,117] rings. In the oxidation of heterocyclic phenols in the presence of the copper(II) complex of a secondary amine, the corresponding *o*-quinones are usually formed with the amine residue in the quinonoid component[118], although in certain cases the heterocyclic fragment of the molecule is aminated[114,117]. Annelation of the quinone ring leads to a redistribution of electron density in the heterocyclic part of the molecule and alters significantly the nature of its reactivity. Isoquinoline quinones, for example, are aminated in the 3-position, although nucleophilic agents usually attack the $C_{(1)}$ atom of isoquinoline.[18]

IV. OTHER INSTANCES OF S_NH REACTIONS

As far as we are aware there are no examples in the literature of the activation of the nucleophilic substitution of hydrogen by SO_2R, CN, and $\overset{+}{N}R_3$ groups. The explanation is probably the tendency of the groups themselves to be split off in the form of anions on treatment with nucleophilic agents.

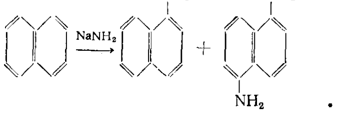
However, there are examples of S_NH reactions in systems activated by the carbonyl or carboxy-group. Thus phenylmagnesium bromide attacks the *o*-position relative to the carbonyl group in the reaction with benzoylmesitylene (XXI), forming 2′-phenylbenzoymesitylene (XXIII). The dihydro-compound (XXII) can be sometimes isolated in small amounts as a side product[119]:



(XXI) (XXII) (XXIII)

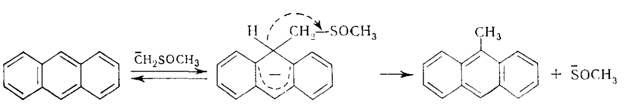
p-Hydroxybenzoic acid mixed with salicyclic acid can be obtained by fusing potassium benzoate with potassium hydroxide[120].

In 1901, Sachs[121] discovered the reaction which is a unique instance of an S_NH process in a non-activated aromatic system: fusion of naphthalene with sodamide leads to the substitution of hydrogen with formation of a mixture of 1-naphthylamine and 1,5-naphthylenediamine:



It is even more surprising that naphthols and naphthylamines, which occur in an anionic form in the presence of bases and should be highly deactivated with respect to nucleophilic attack, undergo similar reactions. However, 1- and 2-naphthols form 5-amino-derivatives, while 1- and 2-naphthylamines give rise to 1,5- and 2,5-naphthylenediamines respectively in yields of 20–50%.

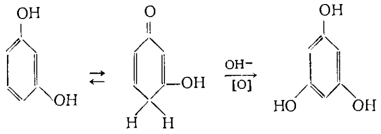
The nucleophilic alkylation of anthracene and phenanthrene by dimethyl sulphoxide and methyl phenyl sulphone[122–124], the carbanions of which are formed under the influence of sodium hydride in hexamethylphosphoramide, was reported in 1966. According to the authors[124], the formation of the final methyl derivatives takes place as a result of a hydride shift and the removal of the sulphinate residue from the anionic σ complex (XXIV):



(XXIV)

It is striking that systems with reduced aromaticity undergo this reaction, while benzene, naphthalene, and thionaphthene do not.

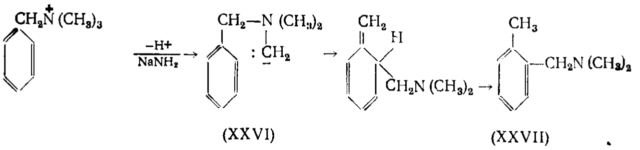
The nucleophilic substitution of hydrogen in the system activated more with respect to electrophilic attack than with respect to nucleophilic attack is represented by the reactions of phenols with alkalis, which lead to the formation of polyphenols with evolution of hydrogen. For example, when resorcinol is fused with alkali, phloroglucinol is formed[120]. This is explained by the fact that a tautomeric form of resorcinol (XXV) enters into the reaction and the latter reduces intrinsically to the substitution of hydrogen in a quinonoid system[50]. The reaction occurs only in the presence of an oxidant[125,126].



(XXV)

Certain intramolecular octet rearrangements and anomalous reactions can probably be classified as S_NH processes. Such intramolecular substitution of the hydride ion occurs, for example, in the Sommelet–Hauser rearrangement[127–129].

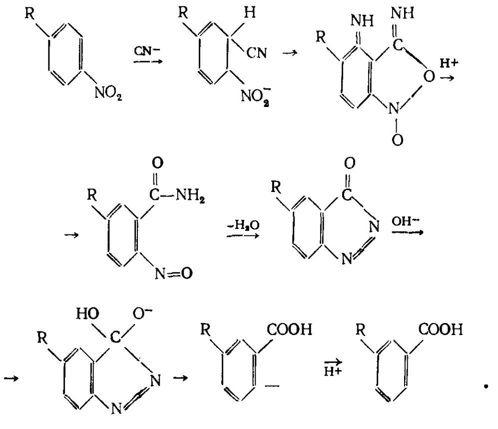
When quaternary benzylammonium salts are treated with strong bases, a proton is abstracted with formation of the ylid (XXVI). The free electron pair then attacks the aromatic ring, which has been activated by the ammonium group whose influence is transmitted via the methylene bridge:



(XXVI) (XXVII)

If the product (XXVII) is remethylated and again subjected to the rearrangement, it is possible to introduce another methyl group into the ring and continue in this way until the hexasubstituted benzene derivative is obtained[129].

The interaction of halogenonitrobenzens with KCN in ethanol at 150°C (the Richter reaction)[130,131] also constitutes essentially an S_NH reaction. Formally, this involves the substitution of the nitro-group, but the COOH group is not found at the site previously occupied by the nitro-group. The mechanism of this reaction has been the subject of a prolonged discussion; the mechanisms proposed by Rosenblum[132] are supported at the present time. It has been incontrovertibly demonstrated that the first stage involves the formation of an anionic σ-complex followed by the removal of hydride-active hydrogen from the latter:



V. S_NH REACTIONS OF AZA-ACTIVATED SYSTEMS

The substitution of a hydrogen atom with its binding electrons in the aromatic cyclopropenylium and tropylium carbonium ions and also in oxa-, thia-, and selena-activated heteroaromatic compounds is described in reviews published in 1974–1975.[6,133]

Aza-activation plays an exceptionally important role in the above processes. In the simplest azine (pyridine), the aza-group exhibits a polarising activity as powerful as that of the exocyclic nitro-group in nitrobenzene. The enhanced reactivity of azine compounds is observed in the *o*-(α-) and *p*-(γ-)positions, where the entropy of activation for electrostatic attraction is greatly enhanced. The nitro-group is known to have a stronger activating influence than the aza-group in the nucleophilic substitution of anionically stabilised species in aromatic systems ($k_{NO_2}/k_{aza} > 1$).[18] However, the intrinsic nucleophilic properties of the aza-group are responsible for its tendency to undergo specific proton solvation, which leads to an increase of reactivity and the reversal of the reactivity sequence: $k_{NO_2}/k_{aza} < 1$.

Only rare instances of S_NH reactions in aromatic aza-systems where neither the reactant nor the substrate is charged are so far known. In the vast majority of cases, the substitution of hydrogen may be achieved by the additional activation by the charge of either the attacking reactant (nucleophile) or the substrate (azine). The papers published up to 1960–1965 were devoted to reactions involving the anionic form of the attacking reactant (H_2N^-, CN^-, and OH^-) and also to organometallic compounds in which the carbon–metal bond is to a large extent polar. These studies have been described in a number of reviews and monographs[2,18,19,134,135]. Whereas only isolated studies using the cationic activation of the azine by its conversion into the *N*-acylammonium form have been made up to that time[136-140], in the last ten–fifteen years systematic investigations have been made and considerable advances have been achieved in the field of the nucleophilic reactions of acylammonium cations[7,9] and also cations arising on formation of azine *N*-oxides[8,141].

This section deals with problems of the activation of aromatic aza-compounds by quaternisation and protonation and also the involvement of nucleophilic substitution of systems not activated by a charge, which have not so far been dealt with in the reviews already published.

1. Quaternary and Protonated Salts

Quaternary and protonated azine salts are on the whole less electrophilic than the corresponding *N*acyl salts[7] or *N*-oxide ethers[8]. Their reduced reactivity is undoubtedly a consequence of the fact that the alkyl group and the proton exhibit electron-donating properties, in contrast to the electron-accepting properties of the acyl or ether residues. Aryl residues occupy an intermediate position between these two types. The use of quaternary and protonated salts is preparatively simpler and in addition makes it possible to introduce them into compounds containing OH, NH_2, and NHR groups, which cannot be done with acyl salts, owing to the transacylation which occurs under these conditions.

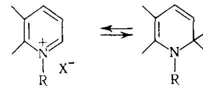
It has been frequently postulated that the mechanism of the S_NH reactions of azines involves "addition–elimination"[1,7-10], but kinetic data[142,143] confirming the validity of these hypotheses have been obtained only in recent years.

The formation of intermediate addition products on substitution of hydrogen in azinium cations can be observed experimentally, as in the corresponding processes with participation of nitro-activated systems and quinones. The profile of the potential energy surface of the delocalisation of the negative charge following the introduction of additional aza-groups or benzo-annelation constitutes a favourable factor, stabilising σ complexes, lowers the energy of their formation and thereby increases the reactivity of the initial azinium cations. For this reason, the manifestation of the higher reactivity of aza- and benzo-azines compared with the simplest azine (pyridine) is to be expected in S_NH reactions and in the substitution of the groups eliminated.

Quaternary salts constitute a very convenient object for study, since the addition product formed is uncharged and is therefore more stable than the classical Meisenheimer anionic complexes. This makes it possible to investigate in detail the structures of such compounds, including X-ray diffraction analysis, which is particularly important for the understanding of the stereochemistry of the transition state[12].

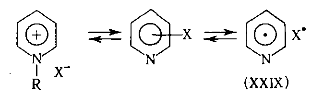
Reactions leading to the substitution of hydrogen under the influence of anionic and anionoid reagents are known in the series of quaternary and protonated salts of azines. Reactions with negatively charged species have been studied in greatest detail. A tendency towards interaction with nucleophilic agents is manifested by the azinium cations within the quaternary salts themselves. A classical example of such an interaction between the cation and anion, accompanied by charge transfer, is provided by alkylpyridinium iodide and its analogues[144-146].

The enhancement of the nucleophilic properties of the counterion in the series $ClO_4^- < C_6H_5SO_3^- < NO_3^- < CH_3COO^- < OCH_3^- < Cl^- < Br^- < N_3^- < OH^- < SCN^- < I^- < CN^- < S_2O_3^-$ [147,148] leads to an equilibrium between anions such as CN^-, SH^-, and OH^- and covalent structures, which is strongly displaced to the right[149-151]. The stability of covalent compounds of type (XXVIII) also increases in the sequence pyridine < quinoline < acridine.



(XXVIII) .

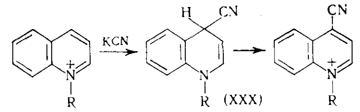
Complexes with partial charge transfer and biradical species, usually arising in an excited state, occupy an intermediate position between the purely ionic salts ($X = ClO_4$ or NO_2) and covalent structures—the so called "cryptosalts"[149] (X = CN or OH).



(XXIX) .

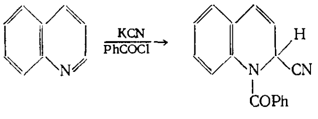
Charge-transfer complexes similar to compound (XXIX) can in all probability play in important role in the mechanism of S_NH reactions.

Alkylpyridinium salts and their analogues readily react with potassium cyanide in an aqueous medium[152-154], forming initially the dihydro-compounds (XXX), which may be oxidised by iodine to the corresponding nitriles[152], for example:



(XXX) .

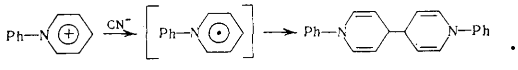
Dihydroquinoline (XXX) is an analogue of Reissert's compounds[155], which arises in the reaction of an acylquinolinium salt with the cyanide ion:



(XXXI) .

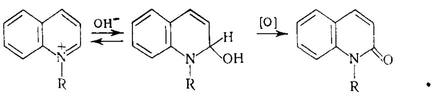
The causes of the formation of the 4-addition [compound (XX)] and 2-addition [compound (XXXI)] products when alkyl- and acyl-quinolinium cations are attacked respectively have not been elucidated[156]. The reactions of the cyanide ion with alkylacridinium[157] and phenanthridinium[158] salts occur similarly. The micellar catalysis by surfactants of the reaction of cyanide with a quaternary salt of nicotinamide[159] has been investigated and it has been established that the rate constants increase in the presence of low concentrations of the detergent and following the addition of zwitterionic compounds.

Certain data concerning the mechanism of the reaction of the cyanide ion with azinium cations have now been obtained. In particular, it has been established that the product of addition in the 2-position is formed initially and then rearranges to the corresponding 4-derivatives[160], which resembles the formation of Servis complexes in the series of aromatic nitro-compounds[15]. When phenylpyridinium chloride was allowed to react with the cyanide ion in an inert atmosphere in an aqueous acetone solution, *N*-phenylpyridyl radicals were detected[161] and the reaction led to the isolation of a dimeric product without nitrile groups:



This led the authors to the hypothesis that the interaction of quaternary pyridinium salts with CN^- proceeds via a one-electron mechanism: in the absence of air, it is completed by the recombination of the intermediate radicals. The presence of oxygen is responsible for another course of the reaction: an addition product is formed, which can then be subsequently oxidised with elimination of the nitrile residue[157].

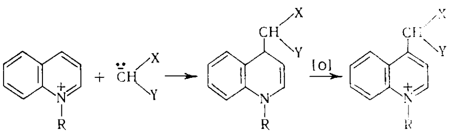
Pozharskii et al. recently demonstrated the substitution by the amide ion of the hydrogen in methylacridinium iodide, which is so far the only example of the involvement of a quaternary salt in the Chichibabin reaction[162]. The final product of the familiar interaction of azinium cations with the hydroxide ion may be regarded as a result of the substitution of hydrogen when the reaction is carried out in the presence of an oxidant, for example potassium hexacyanoferrate(III):



In the absence of an oxidant, there is also a possibility of the formation of oxo-compounds mixed with an equal amount of the dihydro-compound as a result of the disproportionation of pseudobases[163]. Such disproportionation of pyridine and quinoline proceeds via the open-chain form of the pseudobase (derivatives of glutaconaldehyde[164]).

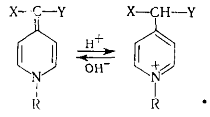
The reactions of carbanions of the type $\bar{C}H_2$–COX include the interaction of pyridinium and benzopyridinium salts with methyl ketones, β-dicarbonyl compounds, cyanoacetic ester, etc. in the presence of strong bases[165-170].

The reactions of CH-active compounds with azinium cations are of interest as models of the addition of acetone and hydroxyketones to diphosphopyridine dinucleotide[171], discovered in 1954. Pyridinium and quinolinium cations usually form 4-substituted products[165,167,169,170], while isoquinolinium[165,172] and acridinium[166,173,174] cations form 1- and 9-substituted products respectively:



Here X = H, $COOCH_3$ or CN and Y = NO_2, CN, $COOCH_3$, or COC_6H_5.

Adducts, which are probably intermediate in the formation of substituted products although this has not been demonstrated kinetically, can be frequently isolated from the reaction mass. The stability of the addition products increases with decrease of the aromaticity of the initial azines: pyridine < quinoline < acridine. Dihydro-compounds are readily oxidised in air[173] and can be dehydrogenated by other oxidants: lead tetra-acetate in benzene, permanganate in acetone, chloranil, etc.[174,175]. In the presence of alkalis, the oxidation of adducts leads to the formation of coloured "dihydrocompounds" (XXXII) of the quinonoid type, which are rearomatised on treatment with acids[165]:



(XXXII)

The methyl groups in the α- and γ-positions relative to the aza-group in heteroaromatic compounds are known to exhibit some CH acidity. It has been shown that these compounds are able to react with the acridinium in the absence of base catalysis[176-179]. However, one cannot rule out the possibility that the catalytic effect is shown by the reactants themselves, which are bases. Methylated heterocycles, both in the form of bases and quaternary or protonated salts, can be made to react with the acridinium cation. In its turn, the substrate can be used also in the form of the protonated salt and, in the presence of active nucleophiles (quinaldine and lepidine), hydrogen can be substituted in the acridine base too. The condensation takes place under oxidising conditions; suitable oxidants are sulphur (melt) and atmospheric oxygen bubbled through a solution in a polar solvent.

Table 2. The rate constants for the methylation of heterocycles by acridine hydrochloride (in DMF, 120°C, bubbling with air).

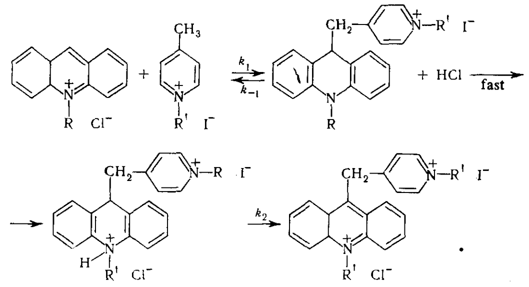
Heterocycle	10^3k, litre mole^{-1} s^{-1}
4-Picoline methiodide	0.50±0.01
4-Picoline ethiodide	0.51±0.01
4-Picoline N-2-propiodide	0.47±0.01
2-Picoline methiodide	0.132±0.007
4-Methylquinoline methiodide	0.50±0.002
2-Methylquinoline methiodide	0.248±0.016
2-Methylbenzothiazole methiodide	0.183±0.003
2-Methylbenzimidazole methiodide	0.031±0.002
Acridine + 4-picoline methiodide	0.062±0.003

This reaction is unusual because it proceeds only in the presence of an oxidant and the addition products characteristic of acridine in an inert atmosphere cannot be detected even in the ultraviolet spectra of the reaction mixtures[142].

The study of the kinetics of the reaction of acridine hydrochloride with the quaternary salts of methylated heterocycles under the conditions of a zero-order reaction with respect to oxygen showed that it is of second order overall and of first order with respect to each reactant. The rate constants are listed in Table 2. The reactions proceed with low activation energies (9–13 kcal mole^{-1}).

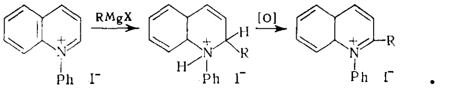
The reactivities of the heterocycles in this reaction (4-methylquinoline > 4-picoline > 2-methylquinoline > 2-methylbenzothiazole > 2-picoline > 1,2-dimethylbenzimidazole) are consistent with the acidities of the protons of the methyl groups based on deuterium-exchange data[180]. Protonation of acridine increases the rate of reaction and the electron-donating properties of the alkyl chain hardly influence the rate.

In many instances the kinetic curves are S-shaped owing to an induction period, which decreases with increase of temperature and the concentrations of the reactants. This shows that the reaction proceeds via an intermediate compound, which is present at a vanishingly low quasistationary concentration.



The example discussed demonstrates the decisive role of the oxidant in both S_NH reactions, where the σ complex is formed at a quasistationary concentration and the substitution of hydrogen can be achieved only in the presence of an oxidant.

As already mentioned, the carbon–metal bond in organometallic compounds, including Grignard reagents, is highly polarised and approaches a linkage of the ionic type. The reactions of alkyl- and aryl-azinium cations with organometallic compounds constitute an example intermediate between their reactions with anions and uncharged species. Quaternary pyridinium salts and their benzo-derivatives combine with Grignard reagents to form dihydro-compounds[181-185], which are mainly unstable and are readily oxidised to the corresponding substitution products[182]:



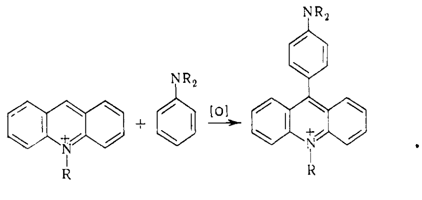
The analogous interaction of benzylpyridinium chloride with cyclopentadienyl-lithium is completed by the substitution of the hydride ion[186].

Among the uncharged nucleophiles used to substitute hydrogen in heteroaromatic cations, mention should be made of alkyl- and aryl-amines and their derivatives, heterocycles with an excess of π electrons, and phenols[187-198]. These are undoubtedly much weaker nucleophiles than anionic reagents. Whereas in the series of acyl salts[7] and *N*-oxide ethers[8], the S_NH reactions of anionoid reagents can be achieved even with pyridine, among the quaternary salts those of quinoline and isoquinoline are inactive[199], although their protonated salts can be made to react in this way[200,201]. The cations whose activity has been increased by benzoannelation (acridine[187]) or by an additional aza-group (diazanaphthalenes[198,202,203]) react smoothly with uncharged nucleophiles, forming adducts or hydrogen substitution products depending on the nature of the substrate.

The quaternary salts derived from acridines, both unsubstituted and containing substituents in the 9-position[204], instantly combine with alkylamines, forming the corresponding acridans. Acridans, containing hydrogen at the geminal site, may be oxidised by an acridinium salt as a result of an intermolecular hydride transfer[205].

The hydride ion is abstracted and substituted in the *N*-alkylacridinium cation following attack by arylamines under oxidising conditions (melt with sulphur, bubbling of air through a solution in dimethylformamide or dimethyl sulphoxide). It has been shown that in the melt with sulphur the reaction does not proceed via a stage involving the preliminary thionation of acridine, sulphur behaving merely as an oxidant[189]. The yields of aminoarylacridinium salts are 80–90%. The side products are acridinone or thioacridinone depending on the experimental conditions.

Arylamines containing various substituents in the ring and in the aminogroup, including arylhydrazones of aldehydes and ketones and carboxylic acid arylhydrazides, may be used in these reactions[206]:



Halogens exhibiting an appreciable *–I* effect lower the reactivity of arylamines; groups with a *–M* effect fully deactivate the nucleophile when they are introduced both in the ring and in the amino-group (Table 3). The basicity of aromatic amines may serve as an indirect criterion of their nucleophilic properties. Amines with a high basicity ($pK_a > 4$) readily react with the acridinium cation; amines with $pK_a = 3.5–2.5$ react but under more severe conditions; compounds with $pK_a < 2.5$ are not reactive.

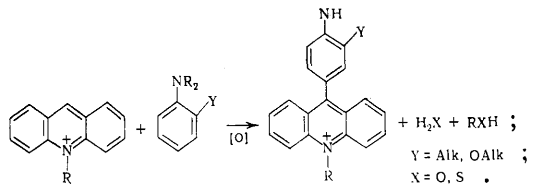
Table 3. The reactions of arylamines with acridine hydrochloride.

Initial arylamine	pK_a	Reaction conditions		Yield, %	
		temperature, °C	time, h	9-aminoaryl-acridine	thio-acridinone
Aniline	4.58	130	2	95	4
N-Monoethylaniline	5.11	120	1.5	92	5
NN-Dimethylaniline	5.06	130	2	94	4
NN-Dipropylaniline	5.29	120	2	90	8
o-Toluidine	4.39	125	2	90	8
m-Toluidine	4.69	120	2	70	20
p-Toluidine	5.13	130	7	25	43
NN-Dimethyl-*m*-toluidine	5.24	135	4	66	28
NN-Dimethyl-*p*-toluidine	—	140	7	*	40
o-Aminophenol	4.47	135	1	85	—
m-Aminophenol	4.30	135	1	95	4
o-Anisidine	4.49	125	2	84	4
NN-Dimethyl-*m*-anisidine	—	125	2	91	—
o-Phenetidine	4.47	125	2	84	10
o-Phenylenediamine	4.74	135	1	80	—
m-Phenylenediamine	4.98	130	1	91	5
o-Chloroaniline	2.64	140	4	25	20
m-Chloroaniline	3.5	135	4	32	34
1-Naphthylamine	3.92	120	1,5	85	5
2-Naphthylamine	3.4	120	2	60	20
m-Nitroaniline	2.47	140	4	*	20
o-Aminoacetophenone	2.22	140	4	*	20
Acetanilide	—	140	4	*	15

*The reaction does not occur; 9-aminoarylacridine was not detected chromatographically in the reaction mixture.

A number of anomalies have been noted in the interaction of arylamines with acridinium salts. Thus phenylhydrazine causes dimerisation of the acridine residues with formation of *NN*-dialkyl-9,9′-biacridanyls[207]. Sterically hindered arylamines behave in an unusual manner. *ortho*-Substituted dialkylanilines undergo dealkylation and monoalkyl derivatives are formed instead of the expected *NN*-dialkylaminoacridinium salts.

The alkyl group split off does not pass to the ring but is eliminated and converted into an alkanethiol when the reaction is carried out in a melt with sulphur or into an alcohol when the oxidant is oxygen[204,208]. The reactions of *NN*-dialkylanilines containing bulky residues give rise to complexes containing three iodine atoms and not to the usual 9-aminoarylacridinium iodides[209]. Such unexpected formation of tri-iodides is probably associated with electron transfer from the electron-donating reactant to the electron-accepting reactant, although one cannot rule out the possibility also of other oxidation-reduction processes, which may lead to the formation of free iodine.



Some data have been obtained for the mechanism of the reactions with arylamines. The primary interaction of the acridinium cation with a dialkylaniline results in the formation of a 1 : 1 charge transfer complex[210], which may be located on the reaction coordinate[199].

The study of the rates of the process demonstrate the absence of base catalysis, the kinetic isotope effect in the reaction with 2,4,6-trideuteroaniline being reduced approximately by a factor of three: $k_H/k_D = 2.28$ (Table 4).[143] Together with the NMR studies on the reaction mixtures, these data show that, as in the reaction with reactive methyl-substituted heterocycles, the oxidative substitution of hydrogen by arylamines proceeds via a stage involving the formation of an intermediate, which probably has the structure (**XXXIII**)§.

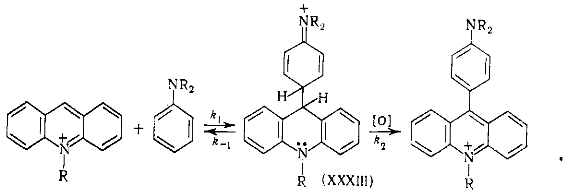


Table 4. The rate constants of the reactions of acridine methiodide with arylamines in DMF on bubbling with air.

Arylamine	Reaction temp., °C	10^2k, litre $mole^{-1}$ h^{-1}	Arylamine	Reaction temp., °C	10^2k, litre $mole^{-1}$ h^{-1}
Aniline	100	0.081	*NN*-Dimethylaniline	100	0.047
Aniline	110	0.124	*NN*-Dimethylaniline	120	0.118
Aniline	120	0.216	*NN*-Dimethylaniline	130	0.180
Aniline	130	0.293	*N*-Methylaniline	120	0.170
2,4,6-Tri-deutero-aniline	120	0.095	*o*-Toluidine	120	0.198

The activation energies are also low in this case. The appearance of a kinetic isotope effect can be explained by the high value of k_{-1}. The steric hindrance arising on

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§The formation of the analogous σ complex of trinitrobenzene with phenol, in which the two species are connected via a C–C junction, has been demonstrated recently by NMR.[211]

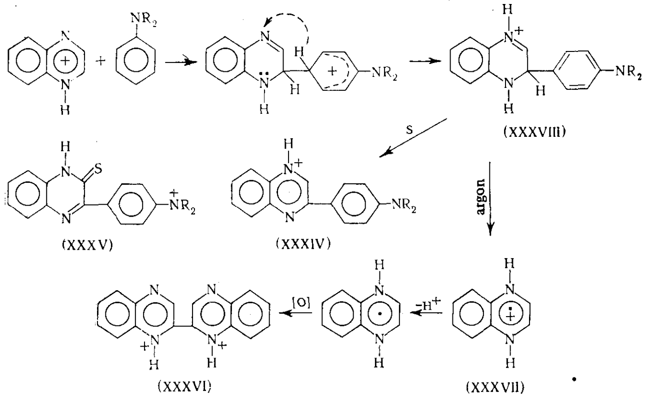
formation of the state (XXXIII) in *ortho*-substituted dialkylanilines can explain their cleavage in these reactions. The dynamics of the interaction of the alkylacridinium cation with five-membered heterocycles, such as indole, with phenols[196] is probably similar to that already discussed.

It was noted above that the introduction of an additional aza-group into the azine molecule activates it with respect to participation in $\mathrm{S_N}$H reactions. Indeed, using quaternary quinoxalinium salts, it is possible to carry out the oxidative subtitution of hydrogen by residues of nucleophilic heterocycles such as pyrrole and indoles[202]. The corresponding 3-methylquinazolinium salts give rise to anomalously stable σ complexes, which are not dehydrogenated by oxidants such as chloranil, iron(III), and sulphur[198]. This manifests the tendency of the 3-alkylquinazolinium cation towards its preferential existence in the form of dihydro-compounds, for example, covalent hydrates[212]. The 1-methylquinazolinium cation does not exhibit a tendency towards interactions of this type[203].

The interaction of protonated salts of azines with uncharged nucleophiles does not differ in principle from the reactions of the quaternary salts. However, one should bear in mind that in this instance there is a possibility of proton transfer from the substrate to the basic reactant, for example an arylamine, and the reactions then proceed with participation of equilibrium concentrations of the reactants. When the reactant is appreciably basic, this can probably constitute an obstacle to such reactions. The principles of additional activation are in this case the same as for quaternary salts and for this reason here too the most reactive compounds are acridine salts—hydrochlorides, sulphates, nitrates, phosphates[191], and salts with organic acids. The yields of the amino-arylation products are nearly quantitative when the oxidant is sulphur or air in dimethylformamide solution, while the yield of the reaction in nitrobenzene, which probably behaves as an acceptor of hydride ions, is about 46%[205]; the yields of acridinylindoles are 64–68%[213] and those of acridinylphosphonates are 70%.[214] In the series of quinoline derivatives nucleophilic hydrogen substitution reactions proceed less satisfactorily; aminoaryl derivatives are formed in yields of about 50%[200] and the yields of quinolinylindoles are 5%.[215] Derivatives of pyridine have not been obtained from its hydrochloride in these reactions.

In the reactions of both protonated and quaternary salts, the successful occurrence of the $\mathrm{S_N}$H processes depends on the correct choice of oxidant. Quinoxaline hydrochloride reacts with dimethylaniline in a melt with sulphur; together with the normal hydrogen substitution product (XXXIV) (14%), this involves the formation of the thiono-derivative (XXXV) (60%). Under argon in dimethylformamide solution, the same reactants give rise to 2,2'-diquinoxaline (XXXVI) only. When the reaction is carried out in air, no products are detected. The appearance in the reaction mass of the radical-cation (XXXVII), detected by ESR, can be explained by the homolytic decomposition of the σ complex (XXXVIII). The inhibition of the reaction by oxygen is most probably associated with chain termination via the formation of a peroxide from the radical-cation (XXXVII).[216]

The different mode of reaction in the presence and absence of oxygen in the present instance and in the cases considered previously[95,157] suggests that many of the reactions, which are usually carried out in air, may lead to other results when they are performed in an inert atmosphere.

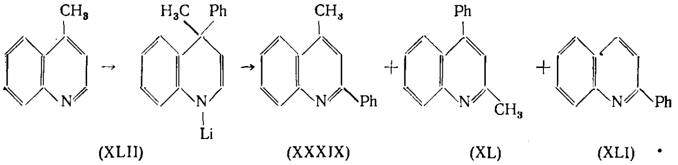


2. Azines which Are Not Activated by a Charge

The vast majority of examples of the substitution of hydrogen in aromatic aza-compounds which are not additionally activated by a charge refer to the interaction of these systems with nucleophiles having a negative charge or with very powerful uncharged nucleophiles such as organometallic compounds. These include in the first place the well known substitution of hydrogen in aza-activated compounds by the amide anion (the Chichibabin reaction) and on fusion with alkalis. These reactions have been considered in detail in a number of reviews and books[134,135]. We shall merely mention that, until recently, the Chichibabin reaction was regarded[217] as a process characteristic of six-membered nitrogenous heterocycles. Simonov and Pozharskii established that many imidazoles containing annelated benzene rings are capable of being aminated by sodamide[135]. This shows that studies on other $\mathrm{S_N}$H reactions in the series of azoles and related systems would be useful.

There is a considerable similarity between the Chichibabin amination and the reactions of aromatic aza-compounds with organometallic reagents. Examples of reactions of azines with organometallic nucleophiles have been discussed in a number of reviews[18,218]. Studies were published in 1967–1971 where the reaction mechanisms were investigated by infrared spectroscopy and NMR[219–222] and the addition products of organolithium compounds, whose formation had been previously postulated, were identified.

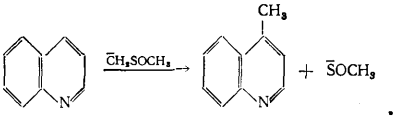
Interesting results were obtained in a study of the reactions of lepidine with phenyl-lithium[219]:



(XLII) (XXXIX) (XL) (XLI)

In this case 2-methyl-4-phenylquinoline (XL) (yield 0.5%) and 2-phenylquinoline (XLI) (yield 3%) are formed together with the main product—2-phenyl-lepidine (XXXIX) (yield 96.5%). A mechanism has been proposed according to which the addition product 1-lithio-4-methyl-4-phenylquinoline (XLII) is formed initially and then rearranges to compound (XXXIX) as a result of the nucleophilic substitution of hydrogen in the 2-position. The nucleophilic substitution of the 4-methyl group leads to compound (XL). Finally the displaced hydride ion may substitute the methyl group in the 4-position with formation of compound (XLI).

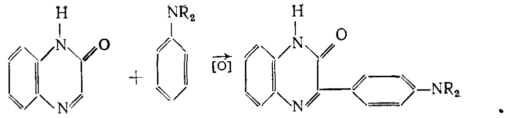
The interaction of free azines with carbanions has been described. Certain instances of such interaction were discussed above[175,176]. Almost all the reactions involve the reactive acridine, which has been shown to form addition products with aliphatic and aromatic methyl ketones in the presence of sodium methoxide[166,174]. The reactions of methyl sulphones[123] and methyl sulphoxides[122,124] with quinoline, isoquinoline, acridine, phenanthridine, and benzoxazole in the presence of sodium hydride are of interest as methods for the preparation of the corresponding methylated azines:



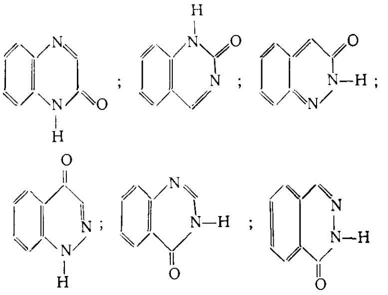
As already mentioned, even the non-activated anthracene and phenanthrene systems are involved in this reaction[122]; however, pyridine, which is more aromatic, proved to be unreactive.

The instances of the nucleophilic substitution of hydrogen where neither the attacking reactant or the substrate are activated by a charge are the rarest reactions in the heteroaromatic series. Whereas the substitution of hydrogen by uncharged nucleophiles (amines, phenols, systems with an excess of π electrons) are usual in the series of quinones, among heteroaromatic compounds these reactions appear to be the privilege of the less aromatic systems with low π-binding energies.

Thus acridine[187] and phenazine activated by the nitrogroup[223] are capable of undergoing direct substitution of hydrogen by arylamines in the presence of an oxidant. The involvement of certain diazanaphthalenones in reactions with arylamines and heterocycles having an excess of π electrons[224,225] has been recently demonstrated, for example:



According to Katritzky[226], diazanaphthalenones satisfy all the criteria of aromaticity, like other azinones, and therefore the instances under consideration can be quite justifiably classified as aromatic nucleophilic substitution reactions. Of the six isomeric diazanaphthalenones



only the first three (quinoxalinone, 2-quinazolinone, and 3-cinnolinone) are capable of undergoing reactions involving the substitution of their hydrogen on treatment with uncharged anionoid agents. Quantum-chemical analysis of the structures of these isomers and the study of the chemical shifts of the substituted protons indicate the absence of any correlation between the chemical shifts and the charge densities, on the one hand, and the reactivities of these compounds, on the other. However, calculations have shown that their reactivities vary in opposition to the energies of radical localisation and are determined by the degree of departure of the system from aromaticity[227].

Examination of literature data shows that these are as yet insufficient to give a complete idea about the criteria of the reactivity and the mechanisms of S_N^H reactions, nevertheless the considerable preparative scope of these reactions, which makes it possible to obtain compounds belonging to a wide variety of classes, should stimulate further theoretical and synthetic studies in this field.

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Thermal Rearrangements of Vinylcyclopropanes

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Various types of reactions of compounds containing vinylcyclopropane groups are considered, particular attention being devoted to data from which the mechanisms of the rearrangements can be inferred.
The bibliography includes 100 references.

CONTENTS

I. INTRODUCTION

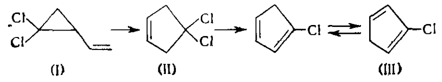
Vinylcyclopropanes are of interest for the investigation of the mutual influence of the cyclopropane ring and an unsaturated group. This influence is illustrated particularly by the relative lability of such systems, which undergo intramolecular rearrangements under various influences (for example, high temperature).

Numerous examples of thermal rearrangements of vinylcyclopropanes are now known. They have been described mainly in the last decade. The types of reactions undergone by the compounds under consideration depend significantly on their structure. In many cases, the isomerisation proceeds with formation of cyclopentenes. When the relative positions of the hydrogen atom in the 1-alkyl substituent and the vinyl group are favourable (*cis*-1-alkyl-2-vinylcyclopropane systems), electrocyclic reactions, including a 1,5-hydrogen shift and yielding dienes, take place. The reactions of divinylcyclopropanes constitute a characteristic example of the Cope rearrangement.

In the present review a systematic account is given of examples of rearrangements of vinylcyclopropanes in accordance with the types of their reactions. Particular attention is devoted to the discussion of studies whose authors attempted to elucidate the mechanisms of the reactions.

II. ISOMERISATION OF VINYLCYCLOPROPANES TO CYCLOPENTENES

The first example of this rearrangement was described in 1959 by Neureiter[1]. In a study of the thermolysis of 1,1-dichloro-2-vinylcyclopropane (I) at 475–500°C, he established that this yields a mixture the main components of which are 4,4-dichlorocyclopentene (II) and 2-chlorocyclopentadiene (III). The latter was obtained via stages involving dehydrochlorination of (II) followed by isomerisation:



(I) (II) (III) .

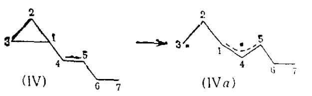
Later it was established that at a lower temperature (200–275°C) the only reaction product is the dichloride (II).[2,3]

Two pathways to the formation of a five-membered ring in this reaction are possible: the biradical pathway (via an intermediate stage involving the opening of the trimethylene ring) and the synchronous pathway (in which there is a simultaneous rupture of the three-membered ring and the formation of a new bond). The latter pathway (a 1,3-suprafacial shift with inversion at the migrating atom or an antarafacial shift with retention of configuration) is allowed on symmetry grounds.

In a number of studies (among which those of Frey must be mentioned), the kinetics of the thermolysis of various substituted monocyclic and bicyclic vinylcyclopropanes were investigated in order to elucidate the mechanism of the rearrangement (Table 1). The results are compared with the kinetic parameters of the thermal rearrangements of the corresponding alkylcyclopropanes in the discussion of the mechanisms of the rearrangements of vinylcyclopropanes. Both biradical[2,3,6,9,10,23,24] and synchronous[4,5,8,12,25] mechanisms for the formation of cyclopentenes have been proposed.

The lower activation energies for the reactions of vinylcyclopropanes compared with the values of E_a for the geometrical and structural isomerisation of alkylcyclopropanes (Table 2) and the low entropies of activation supported the synchronous mechanism[31].

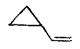
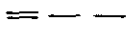
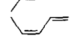
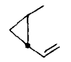
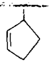
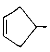
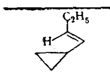
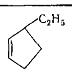
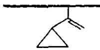
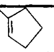
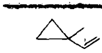
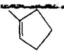
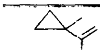
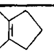
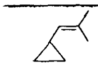
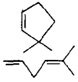
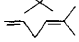
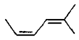
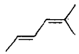
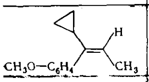
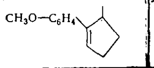
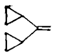
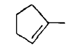
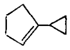
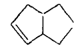
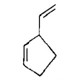
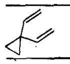
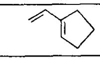
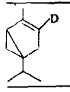
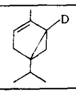
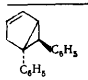
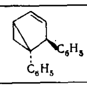
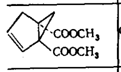
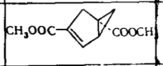
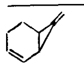
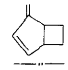
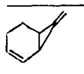
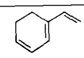
However, the kinetic data obtained could be interpreted also on the hypothesis of the intermediate formation of a biradical. In this case the observed entropy of activation can be attributed to a certain rigidity of the intermediate allyl system. This rigidity is due to the increase of the potential barrier to rotation about the $C_{(1)}-C_{(4)}$ bond from 3.5 to 16.1 kcal on passing from the hydrocarbon (IV) to the corresponding allylically stabilised biradical (IVa):[15]



(IV) (IVa) .

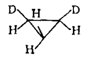
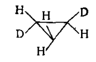
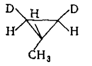
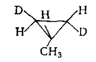
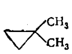
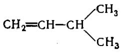
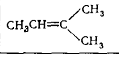
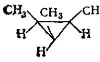
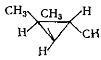
On the other hand, the differences between the activation energies for the reactions of monocyclic vinyl- and alkyl-cyclopropane can be attributed to the involvement of the π electrons of the double bonds in the stabilisation of the biradical. Indeed, the difference between the activation energies for the reactions of 1-methyl-1-vinylcyclopropane (Table 1) and 1,1-dimethylcyclopropane (Table 2), amounting to 13.2 kcal mole^{-1}, is close to the resonance energy of the allyl radical (12.6 ± 0.8 kcal mole^{-1}), which Benson and coworkers determined experimentally[24].

Table 1.* Thermal isomerisation of vinylcyclopropanes to cyclopentenes**.

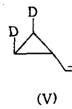
Initial hydrocarbon	Isomerisation products	Temperature, °C	lg *A* (s^{-1})	E_a, kcal mole^{-1}	References
		339—391	13.5	49.60	4
		324.7—390.2	13.6	49.7±0.3	5
		»	14.4	57.3±1.0	5
		»	13.0	53.6±0.8	5
		»	13.9	56.2±0.8	5
		296—328	13.67	48.64	6
		270—290	12.5	45.7±0.6	7
		332.7—373.3	13.79	49.98	8
		332—386	13.89	50.9	9
		313—357	14.11	49.35	10
		325—368	14.14	50.50	11
		350—390	14.00	54.60	12
		»	14.61	56.65	»
		»	13.39	53.00	»
		»	13.25	52.10	»
		332—371	—	50.4	13
		341.9—388.5	14.3	51.1	14
		»	14.0	51.3	14
		271—316	13.36±0.1	44.47±0.26	15
		233—257	12.57	39.6±1.0	16
		201.6—258.6 —	14.33±0.24 14.6	43.41±0.54 44.00	17, 18 19
		144—180	12.6	32.4	19
		132—160	9.69	26.3	20
	 —"—	— 108—138	13.7 13.4	33.5 34.3±1.4	21 22
	 —"—	— 108—138	13.9 17.1	33.9 39.6±1.4	21 22

Thus the kinetic data do not allow an unambiguous choice between the synchronous and biradical mechanisms of the thermal isomerisation of vinylcyclopropanes. In recent years, there has been an increase in the number of facts supporting the biradical reaction pathway.

Table 2. Thermal isomerisation of cyclopropanes.

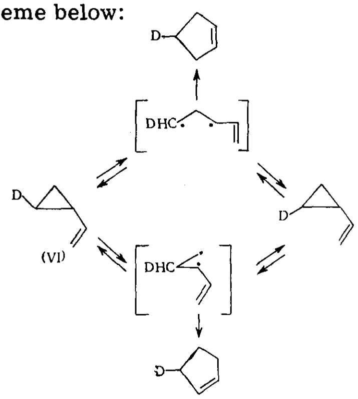
Initial hydrocarbon	Isomerisation products	Temperature, °C	lg *A* (s^{-1})	E_a, kcal mole^{-1}	References
		445	16.41	66.1±0.5	26
	$CHD{=}CH-CH_2D$	»	15.12	65.4±1.1	26
		380—420	15.35	60.5±1	27
	$CH_3CH{=}CHD-CH_2D$	420—475	14.43±0.16	62.3±0.5	»
	$CHD{=}CD-CH_2-CH_3$	»	14.4	62.3±0.5	»
		380—453	15.25	59.42	28
	$CH_2{=}CH-CH(CH_3)-CH_3$	»	14.1	61.8	»
	$CH_3-C(CH_3){=}CH-CH_3$	»	14.1	61.8	»
	 $CH_2{=}CH-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	447—511	15.05	62.6	29
	 $CH_3CH{=}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	»	»	»	»
		395—452	15.78	60.95	30

Willcott and Cargle investigated the thermal transformations of 1-(*trans*-2-deuterovinyl)-*trans*, *trans*-2,3-dideuterocyclopropane (V), and *trans*-2-deuterovinylcyclopropane (VI):



(V)

Here structural isomerisation is accompanied by a degenerate *cis*–*trans* isomerisation [32,33]. It was established that (1) the rearrangement takes place with inversion of configuration at two carbon atoms and (2) the geometrical isomerisation is at least five times faster than the formation of cyclopentenes. The results led to the conclusion that kinetically independent intermediate compounds are formed in the reaction investigated in accordance with the scheme below:



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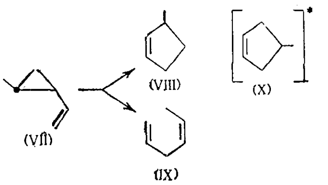
*Tables 1, 3, and 4 list only those examples of the reactions for which the kinetic parameters have been determined.

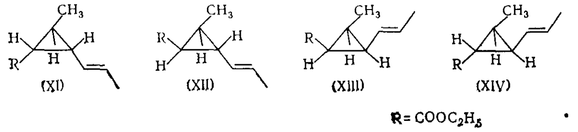
**Quantitative parameters of the simultaneous isomerisation to other olefins are quoted for some of the hydrocarbons.

The study of the thermal isomerisation of *trans*-1-methyl-2-vinylcyclopropane (VII), the reactions of which at 270–330°C proceed with the same activation parameters via two pathways, led to a similar conclusion[6,7]:

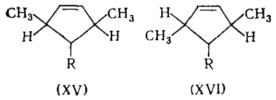


Methylcyclopentene is the "usual" product[†] of the rearrangement of vinylcyclopropanes. The diene (IX) can be formed only from *cis*-1-methyl-2-vinylcyclopropane (this will be discussed in greater detail below). Thus, the isomerisation to cyclopentene is accompanied by *trans*–*cis* isomerisation in this case too.

Data obtained in the study of the thermal transformations of the esters (XI)–(XIV) also constitute evidence against the synchronous mechanism[34]:

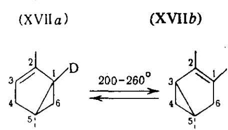


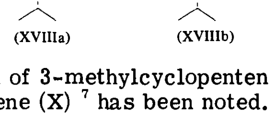
It was found that the above compounds readily undergo isomeric interconversions, the two isomeric cyclopentenes (XV) and (XVI) being also obtained, together with dienes, in various proportions (depending on the structure of the initial vinylcyclopropane).



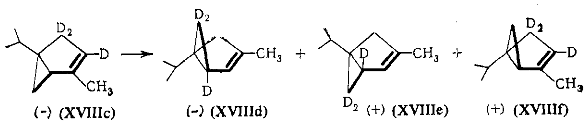
The composition of the reaction product would have been different if one of the possible symmetry-allowed 1,3-sigmatropic shifts occurred. However, according to Mazzocchi and Tamburin[34], the available data are insufficient to rule out the possibility that the reaction proceeds via a combined (concerted and non-concerted) pathway.

A similar rearrangement has been observed also in a series of bicyclic condensed compounds containing a three-membered ring and a double bond in the larger ring. An example of such rearrangements is provided by the degenerate isomerisation of bicyclo[3,1,0]hex-2-ene (XVII)[35] and Δ^3-thujene (XVIII).[17,18,35,36] (At higher temperatures, the three-membered ring is opened—see below.)



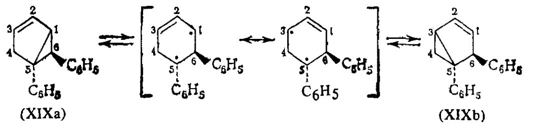


In a detailed study of the reactions of optically active deuterated Δ^3-thujene (XVIIIc) at 240°C, Doering[17] concluded that the reaction proceeds with intermediate formation of biradicals, since the reaction products (XVIII, *d*–*f*) are inconsistent with the predicted formation of the single compound (XVIII*f*) (via a concerted mechanism in accordance with the Woodward–Hoffmann rules):

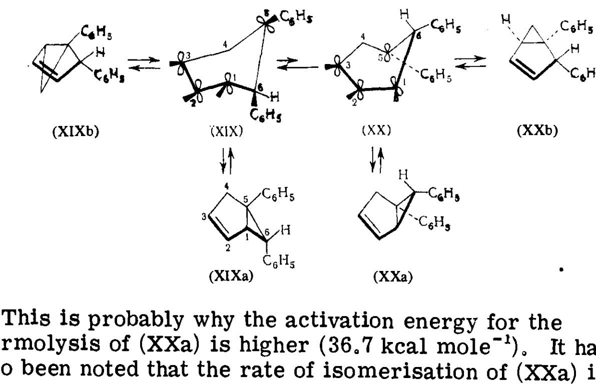


In order to elucidate the pathway whereby vinylcyclopropanes rearrange to cyclopentenes, two methods were used in the above investigations: (1) comparison of the activation parameters for the reaction with those for the simultaneous geometrical isomerisation, for which the mechanism may be regarded as established; (2) comparison of the observed composition of the reaction products and the composition postulated on the basis of the synchronous mechanism. To prove the proposed mechanism, one frequently investigates the stereospecificity of the reaction. Stereospecificity is an invariable consequence of the concerted mechanism. However, stereospecificity alone cannot serve as an adequate evidence for the synchronous mechanism[17].

For example, the stereospecificity of the reversible thermal isomerisation of *trans*-5,6-diphenylbicyclo[3,1,0]hex-2-ene (XIXa) and *trans*-4,5-diphenylbicyclo[3,1,0]hex-2-ene (XIXb)[19,37] can be a result of either the synchronous reaction or a process which may proceed via an intermediate biradical stage in which the rate of closure of the new ring is higher than that of the inversion of the configuration at C$_{(5)}$:



The calculated minimum activation energy for the conversion of (XIXa) into (XIXb) via the biradical (31.5 kcal mole^{-1}) proved to be very close to the experimental value Ea = 32.4 kcal mole^{-1}.[19] The stereospecificity of this reaction is apparently determined by the high energy barrier separating the radicals (XIX) and (XX). In the transformation (XIX) → (XX), there is an appreciable enhancement of the steric interaction between the two phenyl groups, which leads to the breakdown of the coplanarity of the phenyl group and the radical centre at C$_{(5)}$ and hence to decreased conjugation:



This is probably why the activation energy for the thermolysis of (XXa) is higher (36.7 kcal mole^{-1}). It has also been noted that the rate of isomerisation of (XXa) is

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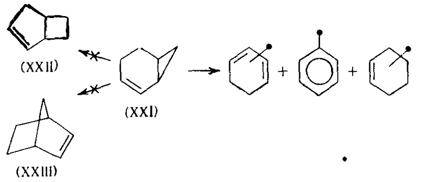
[†] The formation of 3-methylcyclopentene (VIII)[6] and of 4-methylcyclopentene (X)[7] has been noted. Somewhat different activation parameters were obtained in these reactions (see Table 1).

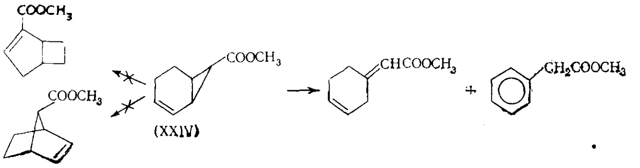
appreciably lower than the rate of reaction of (XIXa). Thus Swenton and Wexler's experimental data[19] confirm the biradical reaction mechanism which they proposed.

The lower activation energies and reaction temperatures for bicyclo[3,1,0]hex-2-ene systems are striking (Table 1). The observed lower activation energy compared with E_a for the rearrangement of monocyclic vinylcyclopropanes has been attributed to the contribution of the strain energy of the five-membered ring (+6.8 kcal mole^{-1})[17,38] and, in the presence of substituents, to the additional stabilisation of the biradical state due to the involvement of the substituents[19,20].

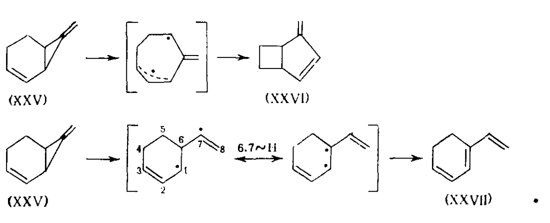
It is noteworthy that the thermal transformations of condensed compounds in the bicyclo[4,1,0]hept-2-ene series {in contrast to bicyclo[3,1,0]hexenes} do not proceed via the mechanism of the rearrangement of vinylcyclopropanes discussed above. Thus a complex mixture of hydrocarbons, the main components of which are methylcyclohexadienes, is formed from bicyclo[4,1,0]hept-2-ene (XXI) at 300–500°C:[39]



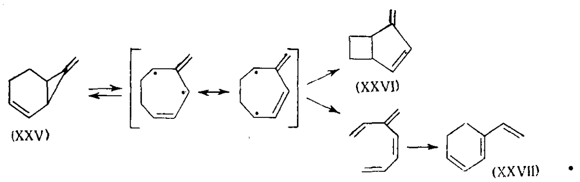
Bicyclo[3,2,0]hex-2-ene (XXII) and bicyclo[2,2,1]-heptene (XXIII), the formation of which would have been expected if there were a rearrangement to the corresponding cyclopentene system, were not detected over the entire experimental temperature range. This applies also to the transformations of the ester (XXIV):[3]



7-Methylenebicyclo[4,1,0]hept-2-ene (XXV), which contains both vinyl and methylenecyclopropane fragments, constitutes an exception in the above series of compounds[21,22]. The methylenecyclopropane fragment is in fact responsible for the specific features of the behaviour of this hydrocarbon. 7-Methylenebicyclo[4,1,0]hept-2-ene isomerises under comparatively mild conditions (at a temperature as low as 110°C) in two independent ways with formation of 4-methylenebicyclo[3,2,0]hept-2-ene (XXVI) and 1-vinylcyclohexa-1,3-diene (XXVII) in proportions of 4 : 1. The ratio of the reaction products changes with increase of temperature above 300°C in favour of the hydrocarbon (XXVII).[22] The activation parameters for the two types of reaction differ appreciably from one another according to one of the investigations (Table 1), which may be due to the fact that the reactions proceed via different transition states, formed in accordance with the mechanism indicated below:



An alternative reaction mechanism corresponds to the identical activation parameters for reactions of both types obtained by Billups et al.[21]:



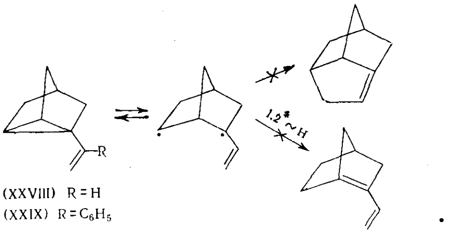
In conclusion of this section, examples of the "anomalous" behaviour of certain vinylcyclopropanes at an elevated temperature will be quoted.

(1) Cases are known where compounds containing the vinylcyclopropane systems do not isomerise to cyclopentenes. These include the following:

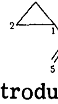
(a) the compounds of the bicyclo[4,1,0]hept-2-ene series already mentioned;

(b) 1-alkyl-2-vinyl- and 1,2-divinyl-cyclopropanes, the rearrangements of which take place in a different way (see below);

(c) the hydrocarbons (XXVIII) and (XXIX) do not change up to 475°C, i.e. under conditions such that even cyclopropanes isomerise. This is probably due to the fact that the rearrangements would necessarily lead to the formation of strained compounds with a double bond at the bridgehead.

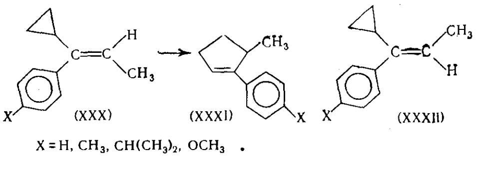


(2) The presence at the $C_{(4)}$ atom of the vinyl group and in the cyclopropane ring of substituents, such as the alkyl group (Table 1), the phenyl[2,41–43], cyclopropyl[2,14,35,44], vinyl[15,25,35,45], and ester[34,46,47] groups and chlorine atoms in the cyclopropane ring[1–3] does not affect the mode of rearrangement of monocyclic vinylcyclopropanes.



At the same time the introduction of substituents at the $C_{(5)}$ atom involved in a double bond has a significant influence on the behaviour of vinylcyclopropanes.

Thus the *trans*-isomer (XXX) is converted almost quantitatively into the substituted cyclopentene (XXXI) in the temperature range 360–390°C. On the other hand, a complex mixture of products, in which the content of the expected cyclopentene does not exceed 20%, is formed from the *cis*-isomer (XXXII); the process is accompanied by intense polymerisation (up to 60%)[41]:



X = H, CH$_3$, CH(CH$_3$)$_2$, OCH$_3$.

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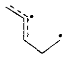
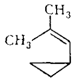
‡ The symbol ~H denotes a hydrogen shift.

This finding has been explained by the fact that the steric interaction of the cyclopropane ring and the alkyl substituent in the *cis*-isomer prevents the formation of a *cis*-allyl biradical of type (XXXIIIa), which precedes cyclopentene. A *trans*-allyl biradical of type (XXXIIIb) should be formed from compound (XXXII).[48,49]

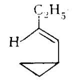

(XXXIIIa)


(XXXIIIb) .

That the transformation of hydrocarbon (XXXIV) has the highest known activation energy of all the thermal isomerisations of vinylcyclopropanes (Table 1) is a consequence of the steric influence of the *cis*-methyl group.



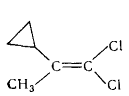
(XXXIV)



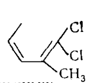
(XXXV) .

On the other hand, the activation energy for the transformation of hydrocarbon (XXXV), containing the *trans*-ethyl group, does not differ from the value of E_a for the unsubstituted vinylcyclopropane (Table 1).

The transformation of 1,1-dichloro-2-cyclopropylprop-1-ene (XXXVI) takes place at 450°C with formation of a complex mixture, the main component of which is the dichloro-derivative (XXXVII):[3]

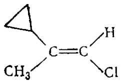


(XXXVI)

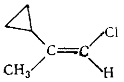


(XXXVII) .

Thus the introduction of two electron-accepting substituents hinders the involvement of the π electrons of the double bond in the opening of the cyclopropane ring. In this case, the usual thermal decomposition of the three-membered ring takes place, namely a reaction which has a higher activation energy than that for the rearrangement of vinylcyclopropanes. The study of the thermal transformations of the isomeric monochloro-derivatives (XXXVIII) and (XXXIX) showed that the electronic influence of the chlorine atom prodominates over the steric influence[3]:

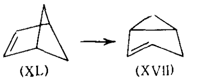


(XXXVIII)



(XXXIX) .

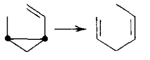
(3) The rearrangement of vinylcyclopropanes is an exothermic reaction (by approximately 25 kcal mole^{-1}) and the reverse reaction is not, as a rule, observed[17]. Systems characterised by a higher strain energy are an exception[50-54]. For example, bicyclo[2,1,1]hex-2-ene (XI) is converted into bicyclo[3,1,0]hex-2-ene (XVII),[50,51] while the reverse process does not take place:


(XL) (XVII) .

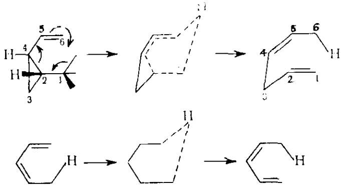
This reaction probably proceeds via a synchronous mechanism, like the 1,3-suprafacial shift with inversion of configuration at the migrating atom, which is confirmed by the stereospecificity[52,54] and the kinetic parameters of the reactions[51,54].

III. ISOMERISATION OF VINYLCYCLOPROPANES INVOLVING A 1,5-HYDROGEN SHIFT

When the steric configuration of 1-alkyl-2-vinylcyclopropanes is favourable, suitable conditions are created for the occurrence of the electrocyclic reaction, involving a 1,5-hydrogen shift and the opening of the cyclopropane ring and leading to isomeric dienes. The simplest case of a rearrangement of this type is the quantitative conversion of *cis*-1-methyl-2-vinylcyclopropane (XLI) above 160°C into *cis*-hexa-1,4-diene (XLII):[6,7,55]


(XLI) (XLII) .

The structural requirements and the geometry of the transition state for the 1,5-hydrogen shift in *cis*-1-alkyl-2-vinylcyclopropanes and *cis*-1,3-dienes are illustrated below:

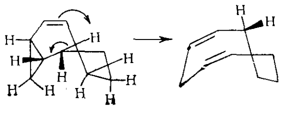


This rearrangement proceeds via a suprafacial mechanism in accordance with the Woodward–Hoffmann rules for the conservation of orbital symmetry[56].

Table 3 presents the activation parameters for the reactions of vinylcyclopropanes occurring with a 1,5-hydrogen shift (data for certain 1,3-dienes are presented for comparison).

It is striking that the activation energy for the above transformation is much lower than the values of E_a for the rearrangement of vinylcyclopropanes into cyclopentenes. The factors A are also lower and correspond in magnitude to the values of A for the Cope rearrangement (Section IV). The low value of A suggests a rigid transition complex in which the free rotations of the methyl and vinyl groups have been lost.

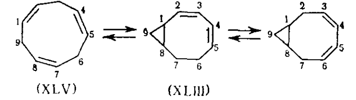
The 1,5-hydrogen shift takes place readily in bicyclo-[n,1,0]olefins (n = 5, 6, or 7), which have a saddle-shaped conformation.



The migrating hydrogen atom is in the *trans*-position relative to the cyclopropane methylene group and this is why a *cis*-diolefin is formed. The thermal opening of the cyclopropane ring in bicyclo[n,1,0]olefins (n = 5, 6, or 7) proved to be a convenient method for the synthesis of *cis*,*cis*-1,4-diene systems.

Thus at 130–200°C bicyclo[5,1,0]oct-2-ene[35,61], bicyclo[6,1,0]non-2-ene[35,60], bicyclo[6,1,0]nona-2,5-diene[62], bicyclo[6,1,0]nona-2,4-diene[60,62,63], and bicyclo[7,1,0]dec-2-ene[17] isomerise smoothly to the corresponding monocyclic compounds.

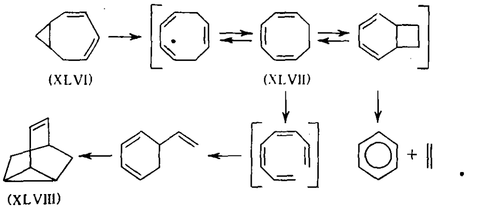
In system (XLIII), the $C_{(7)}-C_{(3)}$ hydrogen shift (a homodienyl shift), competes with the $C_{(6)}-C_{(2)}$ hydrogen shift (a dienyl shift)[60,62,63]:



(XLV) (XLIII) .

Above 160°C the equilibrium is displaced towards the cyclononatriene (XLV). For example, at 170°C we have the ratios (XLV) : (XLIII) : (XLIV) = 93 : 6 : 1.[62]

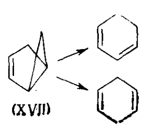
A mixture of hydrocarbons (XLVII) and (XLVIII) and benzene was obtained from bicyclo[5,1,0]octa-2,4-diene (XLVI) at 225°C in accordance with the following reaction mechanism[47]:


(XLVI) (XLVII) (XLVIII)

The corresponding heteroanalogue (XLIX) undergoes a similar isomerisation[64]:

(XLIX)

The non-planar conformation necessary for the 1,5-hydrogen shift is not achieved in bicyclo[n,1,0]olefins (n = 3 or 4). Thus bicyclo[3,1,0]hex-2-ene (XVII) isomerises to a mixture of cyclohexa-1,3-diene and cyclohexa-1,4-diene above 300°C:[7,65–67]

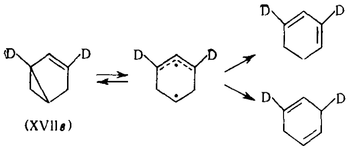

(XVII)

lg$A$ = 14.28 s^{-1}; E_a = 50.2 kcal mole^{-1};

lg$A$ = 14.095 s^{-1}; E_a = 50.2 kcal mole^{-1}.

The activation energies quoted are much higher than the values of Ea for reactions proceeding via a 1,5-hydrogen shift (Table 3). Furthermore, this mechanism does not explain the preferential formation of a conjugated diene on isomerisation (cyclohexa-1,3-diene and cyclohexa-1,4-diene do not undergo thermal isomeric interconversions[68]).

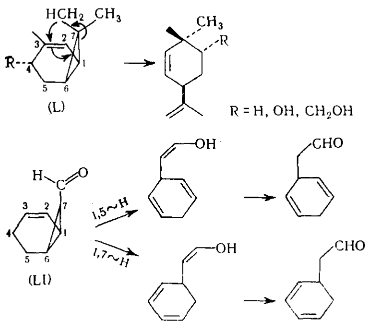
Data obtained in 1973 in studies on the thermolysis of deuterated bicyclo[3,1,0]hex-2-ene (XVIIc) support the biradical mechanism of reactions via a 1,2-hydrogen shift[67]:



(XVIIc)

Evidently, enormous distortions are needed in system (XXI) with n = 4 in order that a transition state be formed for which an electrocyclic reaction involving a 1,5-hydrogen shift is possible. The thermal transformations of bicycloheptene (XXI) take place only via the radical mechanism[39] (see Section II).

Certain substituted derivatives of bicyclo[4,1,0]hept-2-ene [(L) and (LI)][59,69–72] and bicyclo[3,1,0]hex-2-ene[73] are partly isomerised via a six-unit electrocyclic transition state involving a 1,5-hydrogen shift (which is confirmed by the stereospecificity of the reactions and the kinetic parameters):

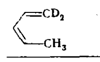
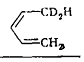
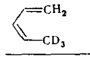
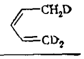
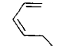
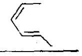
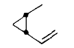
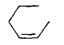
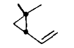
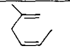
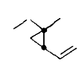
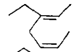
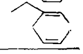
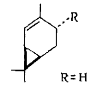
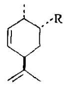
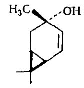
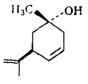
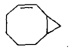
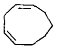
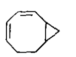
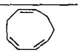
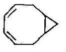


(L)

R = H, OH, CH₂OH

(LI)

Table 3. Thermal isomerisation of *cis*-1,3-dienes and *cis*-1-alkyl-2-vinylcyclopropanes.

Initial hydrocarbon	Isomerisation product	Temp., °C	lg$A$ (s^{-1})	E_a, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	References
		185—205	11.93	36.3	—	—	57
		»	11.86	37.7	—	—	»
		202—245	10.80	32.50	—	—	58
		166—220 170—190	11.03 10.95	31.24 31.1±0.6	30.3 30.2	−11.6 −11.0	6.55 7
		—	11.41	33.54	—	—	31
	 	— —	11.32 11.27	33.7 33.6	— —	— —	31 31
 R = H		200—240	—	—	27.2	−17.2	59
—"— R = OH	—"—	»	—	—	33.0	−8.8	59
—"— R = CH₂OH	—"—	»	—	—	28.6	−6.5	59
		»	—	—	28.0	−6.7	59
		125—150	—	—	31.4	−6	60
	 	125—150 »	— —	— —	29.3 32.5	−7 −5	60 60

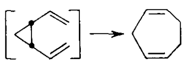
However, these reactions bear only a formal analogy to the isomerisation considered in this Section, since in the case of hydrocarbon (L) the hydrogen atom of the $C_{(7)}-CH_3$ side chain migrates and in the case of aldehyde (LI) the hydrogen atom attached to the carbon atom in the 4- or 5-position relative to the carbonyl group migrates.

IV. ISOMERISATION OF DIVINYLCYCLOPROPANES (THE COPE REARRANGEMENT)

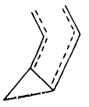
1. *cis*-Divinylcyclopropanes

The isomerisation of *cis*-divinylcyclopropanes, which may be regarded as a special case of the Cope rearrangement of 1,5-dienes, is an interesting example of the [3,3] sigmatropic rearrangement.

The *cis*-isomer of divinylcyclopropane (LII) is so labile that it rearranges to cyclohepta-1,4-diene already under the conditions of its formation[42,49,74,75]:

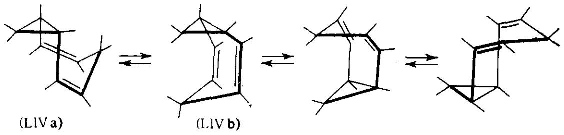

(LII)

Examination of the geometry of divinylcyclopropane leads to the conclusion that the only possible transition state in the rearrangement investigated is the quasi-boat structure (LIII) in which the vinyl groups overhang the plane of the three-membered ring:

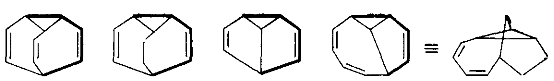

(LIII)

Any other orientations of the vinyl groups would have led to the *trans*,*trans*- or *cis*,*trans*-heptadienes which are not observed. Since only slight changes in the position of the vinyl groups are necessary in the *cis*-isomer in order to attain such a transition state, the rearrangement takes place readily. The reversible degenerate rearrangements of a series of bicyclic and tricyclic unsaturated hydrocarbons belong to the same type of reactions.

The *cis*- and *trans*-isomers of bicyclo[5,1,0]hepta-2,5-dienes (LIVb) and (LIVa) isomerise at room temperature via the stage involving the formation of the thermodynamically less favourable *cis*-form[35,49]:

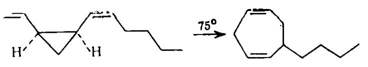

(LIVa) (LIVb)

The allyl groups in bullvalene are rigidly fixed in the cisoid conformation. Rapid reversible isomerisation leads to the approximate equivalence of all the carbon atoms of bullvalene[35,49,76-79]:


(LV) (LVI) (LVII) (LVIII)

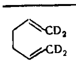
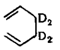
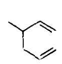
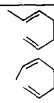
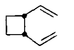
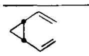
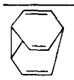
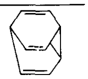
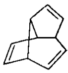
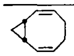
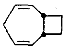
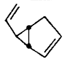
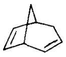
Bullvalene analogues, namely dihydrobullvalene (LVI),[79] semibullvalene (LVII),[80,81] and isobullvalene (LVIII),[82,83] isomerise similarly. Table 4 lists the kinetic parameters of the isomerisation of *cis*-divinylcyclopropanes (data for certain 1,5-dienes and *cis*-divinylcyclobutane are included for comparison). The Cope rearrangement is characterised by comparatively low activation energies and low negative activation entropies.

More stable (stable at room temperature) *cis*-1,2-divinylcyclopropanes are also known: *cis*-1-(*cis*-hex-1-enyl-)2-vinylcyclopropane (LIX)[89] and the bicyclic hydrocarbons (LX),[62,87,90,91] (LXI)[88] (Table 4), (LXII), and (LXIII):

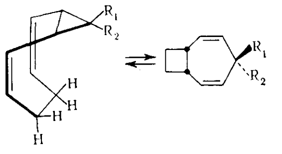


(LIX)

Table 4. Thermal isomerisation of 1,5-dienes and *cis*-divinylcycloalkanes.

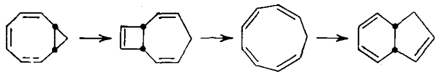
Initial hydrocarbon	Isomerisation product	Temperature, °C	lg$A$ (s^{-1})	E_a, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Ref.
		—	11,1	35.5	—	84
		220—300 220—300	10.5±0.1 10.5±0.1	34.2 35.7	— —	85 86,
		65,4—108,5	10.7	22.4	—11.7	86
 (LII)		5—20	—	—	—5.3	75
 (LV)		10—83 25—123	12.0 12.9	11.8±1,0 12.8±0.1	—5.0 —2.3	77 78
 (LVIII)		11—30	—	—	—10	83
 (LX)		35—48	13.2	25,0±0.5	—	87
 (LXI)		—	11.7	22,9	—7.2	88

The latter isomerise only at 150–180°C. The rearrangement is difficult owing to the steric hindrance by the methyl groups in the *cis*-conformations[89]:



(LXII) R_1=H; R_2=CH_3;
(LXIII) R_1=R_2=CH_3.

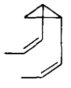
Bicyclo[6,1,0]nonatriene (LXIV) is converted at 90°C into hydrocarbon (LXVI). However, it has been established that the reaction proceeds in succession via a number of stages, each of which takes place with conservation of orbital symmetry[92]. The first stage is the Cope rearrangement to bicyclo[5,2,0]nona-2,5,8-triene (LXV):

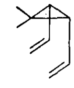

(LXIV) (LXV) (LXVI) .

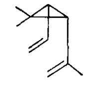
Thus the analogy between the transformations of hydrocarbon (LXIV) and the vinylcyclopropane rearrangement to cyclopentenes, discussed in certain reviews[17,93], is purely formal.

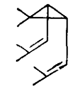
In contrast to unsubstituted divinylcyclopropane, substituted *cis*-divinylcyclopropane systems do not change even under fairly severe conditions.

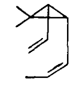
Hydrocarbons (LXVII)–(LXXI), which are stable at room temperature, undergo geometrical isomerisation on heating to 170–180°C, yielding a mixture of *trans*- and *cis*-olefins instead of the expected Cope rearrangement[94–97]:

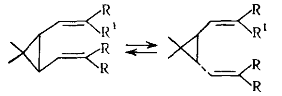

(LXVII)


(LXVIII)


(LXIX)


(LXX)


(LXXI)



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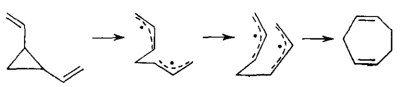
The activation energy observed for the transformation of hydrocarbon (LXX) [E_a = 33 kcal mole^{-1}; lg$A$ (s^{-1}) = 12.4; ΔS = −3.8 e.u.][97] is one of the lowest for the homolytic dissociation of the C–C bonds in cyclopropane (Table 2), which can be accounted for by the involvement of two allyl groups in the stabilisation of the transition state.

The difference in the behaviour of substituted and unsubstituted *cis*-divinylcyclopropanes is due to the steric interactions of the substituents in the transition state.

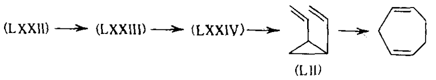
2. *trans*-Divinylcyclopropanes

Since the discovery of the rearrangement of *trans*-1,2-divinylcyclopropane (LXXII)[42] and the determination of its Arrhenius parameters [lg$A$ = 12.09 (s^{-1}) and E_a = 32.10 kcal mole^{-1}],[98] studies on this subject have not been continued. Since the rearrangement hydrocarbon (LXXII) led to the same product as the Cope rearrangement of *cis*-divinylcyclopropane (LII), it has been suggested that the central linkage dissociates owing to the rigid geometry of the cyclopropane ring with formation of the *trans*-allyl biradical (LXXIII), the two allyl components of which then assume the *cis*-positions as in (LXXIV):[35,49]


(LXXII) (LXXIII) (LXXIV) .

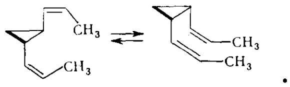
However it remained obscure whether the isomerisation proceeds only via intermediate biradicals or whether biradical (LXXIV) cyclises to *cis*-divinylcyclopropane (LII) with its subsequent rearrangement via a quasi-boat six-unit transition state.

Products containing *trans*-1,2-dialkenylcyclopropane fragments have been isolated in recent years from the oil of *Distyopteris* and the seaweed *Ectocarpus siliculosees*; this aroused more interest in the study of the mechanism of the transformations of *trans*-divinylcyclopropanes. It has been established that at 150–205°C the racemisation of (−)-*trans*-1,2-divinylcyclopropane (LXXII) is accompanied by the geometrical isomerisation to the corresponding *cis*-isomer (LII), which is in its turn rapidly and quantitatively converted into cyclohepta-1,4-diene; here the opening of the cyclopropane ring in the *trans*-isomer is a biradical and not an electrocyclic process[99]:



(LII) .

At 180°C, the *trans*-isomer (LXXV) underwent only geometrical isomerisation with formation of an equilibrium mixture of the *trans*- and *cis*-isomers; the resistance of the latter to the Cope rearrangement was discussed previously[94]:



(LXXV) (LXXII) .

The study of the stereochemical specificity of the thermolysis of other isomeric *trans*-1,2-dialkenylcyclopropanes yielded additional evidence ruling out the possibility of the direct formation of cycloheptadienes from the intermediate *cis*-allyl biradicals of type (LXXIV).[94,100]

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Thus data obtained in kinetic studies on the thermal transformations of vinylcyclopropanes with formation of cyclopentenes can be interpreted both on the basis of ideas involving the synchronous mechanism and on the hypothesis of the intermediate formation of a biradical. However, the results obtained in recent years in studies on the stereochemical specificity of the thermolysis and of the transformations of deutero-derivatives of vinylcyclopropanes are more consistent with the biradical mechanism of the vinylcyclopropane rearrangement.

When the specific configuration of the vinylcyclopropane systems is favourable (*cis*-1-alkyl-2-vinylcyclopropanes and *cis*-divinylcyclopropanes), suitable conditions are created for the occurrence of concerted sigmatropic reactions proceeding via a six-membered cyclic transition state.

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The Solvation of Inorganic Substances and Complex Formation in Non-aqueous Solutions

A.M.Golub

Various views on the nature of the dissolution process are examined and the latter is explained as a consequence of the solvation of the solute. Methods for the determination of solvation numbers and solvating capacities of solvents are analysed and an attempt is made to explain solvation and the influence of the nature of the solvent on complex formation reactions taking into account modern ideas about chemical bonding. The fundamental characteristics of complex formation and inorganic synthesis in non-aqueous and mixed solutions are described.
The bibliography includes 358 references.

CONTENTS

I. INTRODUCTION

The study of the nature of solutions and of the influence of solvents on the reactivity of substances, particularly inorganic substances, has attracted the attention of chemists for a long time. This problem has become particularly urgent, since the majority of chemical engineering processes are carried out in solution and in view of the likely use of lanthanide complexes in non-aqueous solutions[1-3] as lasers. It is very remarkable that the quantum yield for $NdCl_3$ dissolved in a mixture of $SeOCl_2$ with $SnCl_4$ or $SbCl_5$ is ten times higher than for aqueous solutions of neodymium salts[4].

It is well known that the solvent has a significant influence on the state and properties of the solute; however, there is as yet no well-constructed theory on the basis of which one could predict the suitability of a particular solvent for given reactions or for the dissolution of various substances. Nor are there any fairly well-established views concerning solvation phenomena in solutions[5].

According to Mishchenko and Poltoratskii[6], "the nature of ionic solvation forces remains unexplained". On the other hand, there have been numerous studies on the structure of solutions and on complex-formation reactions in non-aqueous systems[7]. It is therefore necessary to analyse the data which have accumulated in order to discover the relation between solvation and complex formation, on the one hand, and to what extent the use of non-aqueous solutions promotes the development of inorganic synthesis, on the other.

II. THE SOLVENT POWER OF SOLVENTS AND THE PROPERTIES OF ELECTROLYTE SOLUTIONS

The old rule "like dissolves in like" is far from being universal, although attempts are sometimes made to revive it even now. Thus, after studying the dependence of the solubility of substances on the properties of the solvent, Semenchenko and then Shakhparonov[8-11] concluded that the relative polarities of the substances involved play a significant role. According to these investigations[8-11], solubility should be highest in those cases where the generalised moments, i.e. the ratios of the dipole moments and the molecular volumes, of the solute and the solvent are similar. Hildebrand and Scott maintain that substances having the same density of interaction energy are miscible[12]. According to Pearson, the so called hard acids or bases dissolve in hard solvents (which themselves behave as hard bases and acids respectively) and soft acids or bases are soluble in soft solvents[13]. However, Pearson's soft acids ($GaCl_3$, I_2, etc.) dissolve readily in alcohols, amines, and hydrazine, which are hard bases. The above rule is to some extent justified in relation to the miscibilities of organic compounds. The Lavoisier rule, developed by Shreder[14], is applicable to many solid non-electrolytes: other conditions being equal, the solubility of solids increases with decrease of their melting point. The rule is usually expressed by the Schroeder–Le Chatelier equation:

$$\lg s = -\frac{\Delta H_m}{RT} + \frac{\Delta H_m}{RT_m}, \tag{1}$$

where s is the solubility, ΔH_m the heat of fusion, T the experimental temperature, and T_m the melting point.

In the case of electrolytes, the solvent power of solvents is usually estimated taking into account their dielectric constants[15,16]. After considering the solubilities of salts in water and some other solvent, Izmailov and coworkers[15,16] established the following relation:

$$\lg \frac{s_{H_2O}}{s_{Solv}} = L\left(\frac{1}{\varepsilon_{Solv}} - \frac{1}{\varepsilon_{H_2O}}\right) + P\left(\frac{1}{\varepsilon_{H_2O}} - \frac{1}{\varepsilon_{Solv}}\right), \tag{2}$$

where L and P are constants and ϵ is the dielectric constant. When a number of assumptions are made, Eqn. (2) can be transformed into

$$\lg s_{Solv} = F + w\varepsilon, \tag{3}$$

where F and w are constants.

The above view was originated by Born[17], who explained dissolution and solvation as a consequence of the ion–dipole interaction[18-24]. According to Born[17], when an ion is transferred from a vacuum into a medium with a dielectric constant ϵ, the solvation energy, equal to the difference between the field energies *in vacuo* and in the given medium, is evolved,

$$E = \frac{z^2e^2}{2r} - \frac{z^2e^2}{2\varepsilon r} = \frac{z^2e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right). \tag{4}$$

Consequently, the solubility of salts should decrease with decrease of the dielectric constants of the corresponding liquids[25,26].

The limitations of the electrostatic concept become evident already in relation to propane-1,2-diyl carbonate, which has a high dielectric constant (ϵ = 69) but dissolves many compounds much less effectively than dimethylformamide (ϵ = 36.1) or dimethyl sulphoxide (ϵ = 48.9). In highly polar nitromethane (dipole moment 3.54 D) the solubility of alkali metal halides is low; transition metal halides are also sparingly soluble in this solvent[27]. On the other hand, acetonitrile, which has almost the same dipole moment (3.2 D) and dielectric constant (38.8), readily dissolves compounds of different classes and even silver nitrate[28], which is sparingly soluble in water.

One cannot explain from this standpoint the low solubilities in water of salts of the type $Cs_2[PtCl_6]$, $[Co(NH_3)_6]$.$[P(Mo_3O_{10})_4]$, and $BaSO_4$, which consist of large cations and anions, the decrease of the corrosion of lead–antimony alloys on passing from water to water–dioxan mixtures[29], the failure of zinc electrode potentials in $ZnCl_2$ solutions in acetonitrile to obey the Nernst equation[30], and the non-uniform variation of the conductivity of aluminium chloride with concentration in butyl ether[31].

In the vast majority of cases, electrolytes behave in non-aqueous solutions differently than in water. For example, thorium nitrate in acetonitrile has a low conductivity; $CuCl_2$ in acetone has a dark-yellow colour[32]; aluminium bromide dissolves in acetone with evolution of heat[33] and the solutions formed darken after a time and their conductivity increases.

The above and also many other data concerning the solubilities of certain salts in alcohols[34-36], dimethylformamide[37,38], acetone[35,39], pyridine[40-42], sulphur dioxide[43], etc.[44,45] show that the dissolution process is determined by the chemical nature of the solvent and the solute rather than by their physical properties. This is why Izmailov[15,16,46] concluded that the dependence of salt solubilities on the dielectric constant corresponding to Eqn. (3) is characteristic only of a series of solvents of the same chemical type, such as, for example, alcohols.

Numerous experimental data have shown that the dielectric constant is not a characteristic which determines solvent power. Thus CuH is insoluble in water but forms a red solution in pyridine (Py), for which ϵ = 12.3, i.e. is lower than for water[47]. Copper iodide also dissolves in this solvent and, when the latter is distilled off, crystallises in the form of $[CuPy_2]I$.[48] The solubilities of many metal halides in pyridine decrease on passing from iodides to chlorides[44].

Hydrazine (ϵ = 51.7) dissolves many salts at 25°C more effectively than does water (ϵ = 81) and liquid HCN (ϵ = 123 at 15.6°C). For example, HgI_2 dissolves in hydrazine more readily than $HgCl_2$ and $Cu(NO_3)_2$ is only sparingly soluble in this solvent[49]. It is difficult to account for the insolubility of CuCN, AgCl, $Ba(NO_3)_2$, $CuSO_4$, HgI_2, and $Ca(NO_3)_2$ and for the low solubilities of AgCN, CdI_2, $CoCl_2$, $HgCl_2$ and $HgBr_2$ in liquid HCN.

The above data show that the formation of the solution and its properties depends mainly on the chemical nature of the corresponding solvents, including stereochemical factors[51]. The rate of dissolution of the solid is higher the lower the activation energy for the transfer of surface species to the solution, which, apart from depending on temperature, is also a function of the strength of bonding between these species and solvent molecules.

Other conditions being equal, substances with a molecular lattice should exhibit the highest solubility and should be followed in this respect by ionic compounds, since, in order to overcome dispersion forces or to dissociate an ionic linkage, it is necessary to expend less energy than for the disruption of atomic or metallic lattices. In particular, it has been noted that the activation energy for the dissolution process is less than 10 kcal mole^{-1} for compounds with ionic bonding[52], while for molecular crystals it is even lower. The dissolution of substances with a molecular lattice is probably preceded by dispersion interaction between molecules of different kinds, which is possible also in the so called indifferent solvents (CCl_4, C_6H_6, etc.).

The first stage in the dissolution of ionic crystals is apparently ion–dipole attraction. The solubilities of salts are therefore usually higher in polar solvents than in non-polar solvents. Substances with a molecular lattice, such as, for example $ThOx_4$, where Ox is the 8-hydroxyquinoline residue, dissolve, while ionic crystals, such as ThF_4, do not dissolve in solvents of the carbon tetrachloride type[53]. Compared with the ionic compound NaNCO, the covalent compound $Hg(OCN)_2$ dissolves more readily not only in alcohols, ethers, and ketones, but also in cyclohexane[54]. For this reason, neutral molecules should be more effectively extracted by solvents immiscible with water, which is in fact observed experimentally[35-57]. It is easier to replace one dispersion interaction by another than to dissociate an ionic linkage or polar molecules into ions.

However, despite its importance when the phases first come into contact, the ion–dipole interaction is not of decisive significance in the general assessment of solvent powers. This is seen from a comparison of the solubilities in water of calcium and cadmium sulphates, the ionic charges and radii of which are the same, and of sodium and copper(I) chlorides in liquid ammonia. Although the radii of the Na^+ (0.95 Å) and Cu^+ (0.95 Å) ions are the same, the solubilities of their salts are by no means identical. Only 3 g of NaCl dissolves in 100 g of ammonia at −35°C,[44,58] while the solubility of CuCl is much higher. In water, alcohols, acetone, etc. the solubilities of these compounds vary in the opposite sense, which cannot be explained by taking into account electrostatic concepts alone.

Sodium perchlorate dissolves readily in ethylenediamine ($\epsilon = 12.9$ at 25°C) and forms with the latter the solvate $NaClO_4.3C_2H_4(NH_2)_2$.[59] On the other hand, this salt dissolves less readily in liquid sulphur dioxide ($\epsilon = 12.35$ at 22°C); the corresponding solvate has not been obtained either[60]. Niobium and tantalum pentachlorides are very sparingly soluble in benzene, carbon tetrachloride, and chloroform[61] and are somewhat more soluble in ethers, ketones (acetone), tributyl phosphate[62], and acetonitrile[63]. For example, it has been shown that, when acetonitrile dissolves niobium pentachloride, it decomposes its polymeric molecules and forms the solvato-complex $[Cl_5NbNCCH_3]$.[63] Zirconium and hafnium tetrachlorides dissolve in many solvents with high solvating capacities[64,65], for example in alcohols and acetonitrile, with which they form the compounds $ECl_4.2Solv$.[64-66] The formation of E–Solv bonds has been confirmed by infrared spectroscopic[67] and thermochemical[68] data. The compounds ECl_4 do not dissolve in liquid hydrocarbons and carbon tetrachlorides, since they do not form adducts with these solvents[70,71]. Aluminium chloride forms more stable solvates and is therefore more effectively dissolved by acetone than by pyridine[58].

III. THE SOLVATION OF INORGANIC SUBSTANCES

It is seen from the above data that the main condition for dissolution is solvation of the species to be dissolved. Solvents with high solvent power in relation to inorganic substances can be divided into two groups: donor and acceptor. The former effectively solvate ions or molecules of the acceptor type and the latter those of the donor type.

Numerous reviews have been devoted to ion solvation[46,72-76], but they are almost exclusively concerned with aqueous systems. In these communications there is unfortunately no indication of the role of the chemical nature of the solvent in the formation of the solvation shells of ions.

Conway and Bockris[74] and also Samoilov[76] developed for aqueous salt solutions interesting ideas concerning primary and secondary ion hydration, suggesting the existence of different types of bonds in solvates. It is quite reasonable that in primary solvation the solute may undergo a significant change in its electrolytic properties. Thus iodine forms with pyridine conducting solutions, from which it is possible to isolate the compound $Py.2I_2$,[77] or more precisely $[IPy][I.I_2]$.

Owing to solvation, the covalent compound $TiCl_4$ dissociates in acetonitrile[78]:

$$2\,TiCl_4 + 4CH_3CN \rightleftarrows [TiCl_3(CH_3CN)_3]^+ + [TiCl_5(CH_3CN)]^-.$$

When $TiCl_4$ dissolves in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), the molecules of the latter are attached to the titanium atom, expelling chloride ions to the outer sphere. This process takes place even more readily with $ZrCl_4$ and $HfCl_4$, which form with DMSO the compounds $ECl_4.9DMSO$.[79] Since the conductivities of dimethyl sulphoxide solutions of ECl_4 are high, they presumably contain the solvato-complexes $[E(DMSO)_8]^{4+}$ or $[E(DMSO)_6]^{4+}$. On being dissolved in tetramethylene sulphone (TMS), cobalt(II) perchlorate forms red conducting solutions, from which it is possible to isolate the compound $Co(ClO_4)_2.3TMS$, whose electronic spectrum resembles that of $[Co(H_2O)_6]^{2+}$.[80]

In contrast to primary solvation, secondary solvation arises as a result of the electrostatic attraction of dipoles or via hydrogen bonding. On the other hand, the formation of the first solvation layer around the solute species apparently plays a dominant role in the dissolution process, since the decrease of enthalpy on dissolution is in fact associated with this factor[82-84].

Since solvation processes in non-aqueous solutions have been studied much less thoroughly than in water, the problem of the relative stabilities of cations and anions in relation to solvation has not yet been solved unambiguously. Gutman[51] suggests that "... the solvation of anions by acceptor solvents usually takes place to a lesser extent than the solvation of cations by donor solvents", and, according to other workers[85-88], anions have higher hydration energies than cations of the same size. The latter is true of potassium, ammonium, rubidium, and caesium fluorides, which dissolve in water with evolution of heat. The same investigators[85-88] nevertheless stipulate that in aprotic solvents, which do not form hydrogen bonds with anions, the latter are less solvated than cations. It is difficult to agree with this view, firstly because in solvents with a high solvent power solvent molecules form the most compact structure around cations[89,90]. Secondly, the energy of the hydrogen bond is low compared with the energy manifested in real solvates, which are in most cases typical complexes.

Comparison of the radii of cations and anions found on the basis of the Stokes law with their crystal-chemical values led Prue and Sherrington[87] to the conclusion that in dimethylformamide and dimethyl sulphoxide cations have a larger solvation shell than anions. The same workers noted that in water and methanol anions have the same conductivities as cations with similar crystal-chemical radii. It has likewise been established that in many other solvents cations are much more solvated than anions[91-95]. On the other hand, for weakly solvated cations, salt solubilities increase in the following sequence of anions:

$$Cl^- < NO_3^- < Br^- < ClO_4^- < I^-,$$

The higher solubilities of potassium and certain other metal iodides compared with their chlorides in hydrazine, liquid sulphur dioxide, acetonitrile, and pyridine are due to the more effective solvation of the iodide ion. The dissolution of KCl in iodine monochloride can be hardly accounted for otherwise than by the solvation of the anion:

$$KCl + ICl = K[ICl_2].$$

This is in fact responsible for the higher conductivity of the solution compared with the pure solvent. When $[(C_2H_5)_4N]Cl$ dissolves in $POCl_3$, a similar interaction takes place[96].

Taking into account the solvation of both the cation and anion, it has been concluded[22] that a total solvation limit exists at which the number of moles of the solvent per mole of the salt is equal to the sum of the coordination numbers of the ions. Since the actual salt solubilities are in many solvents higher than the total solvation limits, an insufficiency of the solvent leads to competition between the ions for the solvating molecules with advantage going to the more active acceptors. According to Mishchenko and Sukhotin[22], the energy of hydration of bivalent cations exceeds by a factor of 5–7 the energy of hydration of anions. A higher degree of solvation is also indicated by many other data[97].

It is clear from the foregoing that the effect of the interionic interaction and structural packing density play an extremely significant role in the solubility of electrolytes in addition to ion solvation. In particular, this leads to the sparing solubility of salts consisting of small cations and small anions. The increase of the solubilities of alkali, alkaline earth, and many transition metal halides in the series from chlorides, to bromides, and to iodides can be accounted for by the decrease of the cation–anion interaction energy.

Even the solubilities of salts comprising the anions SO_4^{2-} and ClO_4^-, which have the same structures, are different. For readily solvated cations, the solubility of perchlorate is appreciably higher than that of sulphates. At 25°C the [saturated?] $NiSO_4.6H_2O$ solution contains 29.36% of the salt and the [saturated?] $Ni(ClO_4)_2.6H_2O$ solution 52.87%;[45] this is due to the different strengths of binding of coordinated water to their anions[98].

Thus the solubility of salts depends also on the mutual substitution of anions and solvent molecules in the first and second solvation layers of the cations owing to the different abilities of the anions to form covalent linkages with the cations and different strengths of the hydrogen bonds between a solvent molecule in the solvato-complex and a free solvent molecule, on the one hand, and between a coordinated solvent molecule and an anion, on the other. If the latter predominates over the former, then, when the contribution of the covalent component to the interionic interaction is appreciable, the salt will dissolve less effectively.

For the majority of chlorides, the strength with which water, dimethylformamide, dimethyl sulphoxide, and even alcohol molecules are bound to metal cations is greater than that for the chloride ion. For this reason, the molecules of these solvents displace chloride ions from the coordination spheres of many complexes[99]. Dimethyl sulphoxide is capable of substituting even covalently bound iodide ions; SbI_3, BiI_3 and PbI_2 form conducting solutions in this solvent[100].

The different capacities of salts for dissociation in different solvents are well known; they have in fact led to the concept of differentiating solvents[101]. Later, Parker[85], who gave preference to electrostatic interaction and hydrogen bonding, considered only two groups of solvents in his assessment of their different behaviour with respect to electrolytes: protic and dipolar aprotic solvents. However, although this approach has been successful in a few instances, it is too narrow and Miller and Parker therefore attempted to reconcile the differentiating action of solvents with solvation effects[86]. They put forward the following hypothesis: the degree of solvation of anions by protic solvents decreases with increase of their radii:

$$OH^-, F^- > Cl^- > Br^- > N_3^- > I^- > NCS^- > ClO_4^-,$$

while the degree of solvation by aprotic solvents decreases in the opposite sequence. In the former case, the strong solvation can be accounted for by the enhanced ability of the anions to form hydrogen bonds with small anions and in the latter by the polarising action of the aprotic dipoles on the large anions. Consequently, the greater the polarity of the solvent the stronger its interaction with anions (particularly large anions). Nevertheless, this hypothesis conflicts with many factors. In fact, the lower solubilities of many salts in nitromethane compared with acetonitrile (see Section II) are due to the greater ease of formation of salt solvates in acetonitrile and not to the difference between the polarities of their molecules[102]. In conflict with Miller and Parker's hypothesis[86], in acetone the silver ion combines more strongly with the iodide ion than with the chloride ion[103] and the solubility of metal halides in ammonia (a protic solvent) increases on passing from fluorides to iodides[51]. Furthermore, among the hydrates $NaHal.2H_2O$, $NaI.2H_2O$ is the most stable, while KI does not form stable hydrates at all. Consequently the effect of salt solvation depends more on the nature of the cation than on that of the anion. Miller and Parker's explanation of solvation processes and solubility is based on an electrostatic concept, which, however, cannot be adopted without significant improvements. From the point of view under consideration, anions of the F^- type should interact vigorously with aprotic solvents, since they have comparatively high field strengths; for this reason, LiF should be more soluble than KF even in water, which is not the case.

IV. THE QUANTUM-CHEMICAL ASPECT OF SOLVATION

The majority of known instances of high solubilities of inorganic substances in various solvents[57,67,77-80] cannot be explained without taking into account the donor–acceptor interaction of solvent molecules with both ions and neutral molecules of the solute. An intense absorption band at 3000 Å, indicating the occurrence of interaction between the system components, has been observed even for a solution of iodine in benzene[104]. The formation of a solvato-complex in this solution is also indicated by the increased dipole moment (1.8 D)[105] caused by charge transfer from benzene to iodine[105,106].

If it is assumed that this complex exists in two mesomeric forms, i.e.

$$C_6H_6 \cdot I_2 \leftrightarrow C_6H_6^+ - I_2^-,$$

then the system in the ground state can be described by a wave function of the following type:

$$\psi_N = a\psi_0(C_6H_6 \cdot I_2) + b\psi_1(C_6H_6^+ - I_5^-). \tag{5}$$

Since the C_6H_6–I_2 bond is weak, the relation between the coefficients a and b is given by the inequality

$$a^2 \gg b^2. \tag{5a}$$

For the excited state, in which the ionic form of the complex should predominate, the expression defining the wave function ψ_E is similar to Eqn. (5), but the coefficients a' and b' are different and the second term $b'\psi_1(C_6H_6^- - I_2^+)$ has a minus sign. The following relations hold between the coefficients a and b and between a' and b':

$$\begin{gathered} a^2 + b^2 + 2abS_{01} = 1; \\ a'^2 + b'^2 - 2a'b'S_{01} = 1, \end{gathered} \tag{5b}$$

where S_{01} is the overlap integral for the wave functions ψ_0 and ψ_1, which is proportional to the interaction integral between the orbital of the solvent molecule and the orbital of the solute species.

Using the Schroedinger equation, the ground state of the solvato-complex can be represented by the relation

$$H(a\psi_0 + b\psi_1) = E(a\psi_0 + b\psi_1), \tag{6}$$

where H is the Hamiltonian and E the energy. The following equations can be obtained by the variational method:

$$\begin{gathered} a(E_0 - E) + b(H_{01} - ES_{01}) = 0; \\ a(H_{01} - ES_{01}) + b(E_1 - E) = 0, \end{gathered} \tag{7}$$

where $E_0 = \int\psi_0 H\psi_0 d\tau$, $H_{01} = \int\psi_0 H\psi_1 d\tau$, and $E_1 = \int\psi_1 H\psi_1 d\tau$. The expressions

$$E = E_0 - \frac{(H_{01} - ES_{01})^2}{E_1 - E}; \tag{7a}$$

$$\frac{b}{a} = \frac{H_{01} - ES_{01}}{E_1 - E}, \tag{7b}$$

can be found from Eqn. (7). To facilitate the calculation, it is assumed that the degree of charge transfer in the ground state of the solvato-complex defined by the wave function ψ_N is low. E can then be replaced by E_0 in Eqns. (7a) and (7b):

$$E_N = E_0 - \frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}; \tag{7c}$$

$$\frac{b}{a} = -\frac{H_{01} - E_0S_{01}}{E_1 - E_0}. \tag{7d}$$

The energy of the solvato-complex E_N in the ground state is equal to the heat of its formation from the components; E_0 is the energy of the electrostatic interaction between the solvent and solute molecules. The second term in Eqn. (7c) defines the covalent component of the A–Solv linkage. For the complex $I_2.C_6H_6$, both terms in Eqn. (7c) are comparable in magnitude. For more stable solvato-complexes, E_0 is very low and may be neglected. The heat of formation of the complex is then given by the expression

$$\Delta H = -\frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}, \tag{8}$$

or, after substituting Eqn. (7d),

$$\Delta H = -(E_1 - E_0)\frac{b^2}{a^2}. \tag{8a}$$

The transition from the ground to the excited state, to which corresponds the characteristic absorption band of the complex $I_2.C_6H_6$, is accompanied by electron transfer from the benzene molecule to the iodine molecule:

$$h\nu = E_E - E_N, \tag{9}$$

which transforms into the following expression when account is taken of Eqn. (7c) and the analogous expression for the energy of the excited state E_E:

$$h\nu = (E_1 - E)\left[1 + \left(\frac{b'}{a'}\right)^2 + \left(\frac{b}{a}\right)^2\right]. \tag{9a}$$

The expression for the energy $h\nu$ of the charge-transfer band of the solvato-complex can also be formulated in a different way:

$$h\nu = I_{C_6H_6} - F_{I_2} + J, \tag{9b}$$

where $I_{C_6H_6}$ is the ionisation potential of the benzene molecule, E_{I_2} the electron affinity of the I_2 molecule, and J a constant.

The energy $h\nu$ is related to the stability of the solvato-complex. For a given solute, for example, iodine, there is a linear relation between $h\nu$ for solvates formed with different solvents and their ionisation potentials.

As stated above, the nature of the interaction between the solute and the solvent can be inferred also from the change in the dipole moment of the solution. Thus, in a benzene solution of iodine, the admixture of $C_6H_6^+$–I_2^- to the ground state explains the polarity of the complex[107].

The dipole moment of the solvato-complex in the ground state is defined by the relation

$$\mu = e\int\psi_N \sum r_i d\tau, \tag{10}$$

where e is the electronic charge and r_i the vector-distance of the ith electron. Taking into account Eqns. (5) and (5b), Eqn. (10) can be written in the following form:

$$\mu_N = a^2\mu_0 + b^2\mu_1 + 2ab\mu_{01}, \tag{10a}$$

where μ_0 and μ_1 correspond to Eqn. (10) and $\mu_{01} = e\int\psi_0\Sigma r_i\psi_1 d\tau = 1/2S_{01}(\mu_0 + \mu_1)$. Ultimately one obtains

$$\mu_N = a^2\mu_0 + b^2\mu_1 + abS_{01}(\mu_0 + \mu_1). \tag{10b}$$

Taking into account Eqn. (5b) and the known dipole moment of the solvato-complex (μ_N), the overlap integral S_{01}, the induced dipole moment (μ_0), and the dipole moment of the solv$^+$–A$^-$ state of the solvato-complex (μ_1), it is possible to calculate from Eqn. (10b) the wave function coefficients a and b. For complexes of the type $I_2.C_6H_6$, the dipole moments of the components are assumed to be zero ($\mu_0 = 0$) and $\mu_1 = er$. Having adopted $r = 3$ Å, calculation yields $\mu_1 \simeq 15$ D. If the overlap integral $S_{01} = 0.1$, μ_N for the solvato-complex is equal to the dipole moment of the A = Solv linkage or

$$\frac{\mu_{A\text{-Solv}}}{er} = b^2 + abS_{01}. \tag{10c}$$

Eqn. (10c) expresses the degree of charge transfer in Solv$^+$–A$^-$. It has in fact been shown in this way that the increase of the dipole moment in complexes of the type $I_2.C_6H_6$ is caused by charge transfer.

When the coefficients a, b, a', and b' and the overlap integral S_{01} have been calculated with the aid of Eqns. (5b), (8a), and (9a), then, using the experimental values of ΔH and $h\nu$ (for different values of $E_1 - E_0$), it is possible to estimate the dipole moment of the solvato-complex. For example, it has been found that $\mu_N = 2.1$ D for $I_2.O(C_2H_5)_2$ when $E_1 - E_0 = 4.2$ eV and $r = 3.0$ Å, which agrees well with experiment (1.9 D).[108] Thus, quantum-chemical calculations have shown that the solvation process is accompanied by a redistribution of electrons characteristic of chemical interaction.

Bernal and Fowler[23] already noted that the solvation energy of a given cation approaches the overall ionisation potential of the corresponding atom. Although the authors adhered to the electrostatic point of view, they nevertheless explained this fact correctly by the return of the missing electrons to the ion (via none other than a donor–acceptor interaction). The validity of this conclusion also becomes evident when the solvation effects for ions bearing the same charges and having similar radii are compared. For example, the solvation energies of Cd^{2+} (0.92 Å) and Ca^{2+} (0.94 Å) are respectively 532 and 346 kcal g-ion^{-1} in ammonia, 430 and 367 kcal g-ion^{-1} in water, and 412 and 309 kcal g-ion^{-1} in formic acid[46]. A similar difference between solvation energies has been observed for Na^+ and Ag^+.[109]

The high solvation energies of cadmium, zinc, and silver ions in ammonia, water, and other electron-donating solvents can be more correctly attributed to the formation of coordinate bonds[81,92,109] rather than to a simple ion–dipole interaction. This is particularly evident from the fact that high solvation effects are observed for cations which usually behave as active complex-forming agents. A similar view has been defended also by other investigators[13,110], who identify solvation with interaction between Lewis acids and bases. However, according to Pearson[13] the bonds formed by Al^{3+}, La^{3+}, Ti^{4+}, Cr^{3+} and other so called hard acids with water, alcohols, and amines are electrostatic, which conflicts with experimental findings.

Solvents with a high donor capacity usually form stable solvato-complexes with cations, as a result of which conducting systems are produced[77-80]. For example, many compounds and even metals[111] which are insoluble in water dissolve in liquid ammonia; on the other hand, calcium chloride is almost insoluble in this solvent[112].

Since the ionic component of the bond does not exceed 50% even in compounds of the MgO type[113], in the solvato-complexes $[Zr(DMSO)_6]^{4+}$, $[Ag(CH_3CN)_2]^+$, etc. its contribution is even smaller. According to some data[114-116], the solvation energy cannot be reliably calculated on the basis of the electrostatic model. The interaction of solute species with solvent molecules can be regarded as ordinary complex formation. Solvation and the properties of solvato-complexes can then be reliably accounted for by the molecular orbital method. In fact, the ion solvates formed in solution can be described by a set of wave functions of the central ion (sp^3d^i) with certain hybrid functions of the solvent molecules:

$$\psi = a\psi_c + b\Phi, \tag{11}$$

where ψ_c are the wave functions of the atomic orbitals of the central atom involved in the formation of bonds and Φ is an average wave function of the solvent molecules attached to the central atom. The solvates of the simplest ions are usually more susceptible to a quantum-chemical interpretation. For example, calculations on the aquo-complexes of lithium and sodium by the LCAO-MO method have been carried out in a number of studies[117-121] and some investigators[119,120] examined only the simplest systems $Li...OH_2^+$, $Na...OH_2^+$, and $H_2O...Li...OH_2^+$.

Calculations have been made[122] by Hoffmann and Lipscomb's method[123] for different internuclear distances and it has been found that the equilibrium distances for Li^+ and Na^+ are appreciably lower than the sum of the crystal-chemical radii of the M^+ ions and water molecules for all values of m in $M(H_2O)_m^+$, which indicates an appreciable contribution of the covalent bond character in these aquo-complexes. The internuclear distances for the potassium aquo-ion are closer to the sum of the crystal-chemical radii. However, it appears somewhat strange that the hydration shells of lithium consisting of six molecules and those of sodium and potassium consisting of eight molecules are more favourable than the tetrahydrate and hexahydrate shells respectively.

Unfortunately, at the present time quantum-chemical calculations on solvation have not gone beyond the limits of aqueous systems. In contrast to water, certain non-aqueous solvents can form π bonds in addition to σ bonds with solute ions or molecules. In this case, the atomic orbitals of solute molecules should be used to calculate yet another molecular wave function Φ', which may combine with the atomic functions of the central ion ψ_c on formation of a π bond. Evidently solvents of the second type, such as, for example, DMSO, should possess an enhanced solvent power.

Chatt[124] took a view similar to the concepts just described; he believes that the enhanced solubilities of certain transition and d^{10} metal salts in π-acceptor solvents can be accounted for by the presence of the weakly held external d^i electrons of the cation. Using these ideas, it is possible to explain many instances of different types of behaviour of salts in different solvents[125-127], for example, the behaviour of $CaCl_2$ and $ZnCl_2$ in $POCl_3$.[127]

The solvent power and the dissociating capacity of the solvent should depend on the relative energy levels of the electrons of solvent molecules and the corresponding ion making the greatest contribution to the bonds formed.

V. DETERMINATION OF SOLVATE-ION NUMBERS

The study of mixed solutions is extremely fruitful in the determination of the composition of solvates. It is then possible not only to establish the composition of the solvent but also to estimate the relative capacities for solvation of a particular pair of solvents and to show which of them interacts with the solute in the presence of the other. The method of solubility has also proved useful in such cases[128-130].

In a mixture of two solvents, one of which hardly dissolves the given substance A and the other readily dissolves it, equilibrium is established following saturation:

$$\mathrm{A} + m\,\mathrm{Solv} \rightleftarrows \mathrm{A}\cdot m\,\mathrm{Solv}.$$

The constant

$$K = \frac{[\mathrm{A}\cdot m\,\mathrm{Solv}]}{[\mathrm{Solv}]^m} \tag{12}$$

is a quantitative characteristic of the capacity of the substance for solvation by the given solvent in the presence of the other. By taking logarithms in Eqn. (12), we obtain the relation

$$\lg[\mathrm{A}\cdot m\,\mathrm{Solv}] = m\lg[\mathrm{Solv}] + \lg K, \tag{12a}$$

which represents a straight line with a conventional slope m. Assuming that $[\mathrm{Solv}] = lc_{\mathrm{solv}}$, where l is a proportionality coefficient and c_{solv} the overall concentration of the solvent, it is possible to determine the solvation number via a combined graphical and analytical method and then also the equilibrium constant

$$K = \frac{[A\cdot m\,\mathrm{Solv}]}{\{c_{\mathrm{solv}} - m[\mathrm{A}\cdot m\,\mathrm{Solv}]\}^m} \tag{12b}$$

itself.

By studying the solubility of $CuCl_2$ in dioxan–solvent (alcohols, dimethylformamide, water) mixtures, it was found that $m = 2$. Table 1 presents the solvation numbers found by the solubility method for a series of other salts. In most instances these numbers agree with the usual coordination numbers of the cations. The lower values of the solvate-ion numbers suggest that salt anions and in some cases also molecules of the second solvent enter into the coordination sphere.

Table 1. The solvation numbers of salts based on their solubilities in dioxan–solvent systems.

Salt	Solvent					References
	H_2O	CH_3OH	C_2H_5OH	DMF	CH_3COCH_3	
$Pb(NO_3)_2$	4; 6	—	—	—	—	129
$MgSO_4$	6	—	—	—	—	131
$CaSO_4$	4; 6	—	—	—	—	131
$MgCl_2$	—	4; 6	4; 6	4; 6	—	12
$CaCl_2$	—	4	3	4	—	128
$NiSO_4$	6	—	—	—	—	131
$CuSO_4$	4; 6	—	—	—	—	131
$NiCl_2$	—	2; 4	2	2; 4	—	132
$CoCl_2$	—	2; 4	—	2; 4	—	128
$MnCl_2$	—	2; 4	—	—	—	131
$ZnSO_4$	6	—	—	—	—	131
$CdSO_4$	4; 6	—	—	—	—	131
$ZnCl_2$	—	2	2	2	—	131
$CdCl_2$	2; 4	—	2	2	—	130
$AlCl_3$	—	—	—	1	1	133

The solvation numbers of undissociated molecules or salts with weakly solvated anions can be most effectively determined by this method. On the other hand, when the salt solvation proceeds in accordance with equilibrium

$$AB_l + n\,\text{Solv} \rightleftarrows A \cdot m\,\text{Solv}^{+l} + l\,B\,i\,\text{Solv}^-,$$

Eqn. (12a) becomes

$$\lg[A \cdot m\,\text{Solv}^{+l}] = \frac{n}{l+1}\lg[\text{Solv}] + D, \tag{13}$$

where D is a constant. In this case the plot based on Eqn. (13) yields the slope

$$\frac{n}{l+1} = \text{slope}, \tag{14}$$

and hence gives only an approximate idea about the solvation of the salt. In order to determine the solvation number of the cation, it is necessary to have additional data concerning the number of molecules i of the solvating solvent attached to the anion. Then,

$$m = \text{slope}\,(l+1) - i. \tag{14a}$$

To determine the solvation number in mixed solvents, one can sometimes use successfully also the spectrophotometric method[132] in conjunction with the Bjerrum procedure[135] or by plotting the simpler relation

$$\lg\frac{D_x}{D_{\max} - D_r}\, m \lg[\text{Solv}] + \lg K, \tag{15}$$

where D_X and $D_{\max}$ are the optical densities of solutions with partial and complete solvation of the solute and

$$K = \frac{[A \cdot m\,\text{Solv}]}{[A][\text{Solv}]^m}. \tag{16}$$

The compositions and formation constants of the dimethylformamide solvates of $CoCl_2$, $NiCl_2$, and $CuCl_2$ in methanol and ethanol were determined by this method[136,137]. It was found that $m = 4$ (moderate DMF concentrations) and $m = 6$ (high concentrations of the solvating solvent) for the first two salts. Under analogous conditions, $m = 2$ and 4 for $CuCl_2$.

In a spectrophotometric study of UO_2Cl_2 solutions in a carbon tetrachloride–tributyl phosphate (TBP) mixture, plots based on Eqn. (15) established the existence of the solvato-complexes [UO_2Cl_2.3TBP] and [UO_2Cl_2.2TBP].[138] The addition of two molecules of pyridine to $CoCl_2$ was established by the same method in the presence of acetone[139,140]. The solvation numbers have been determined spectrophotometrically in a number of investigations[141-145]. Those of neodymium, amounting to 6–8[144] and 4[145], have been found for aqueous alcoholic solutions of $NdCl_3$. The latter number must be regarded as too low, since the solvation shell of neodymium probably incorporates alcohol molecules as well as those of water[140,147]. Other literature values of the solvation numbers of neodymium are 6[148] and 8–9.[149-151]

In order to determine the composition of solvato-complexes by the Bjerrum method, the average solvation number $\bar{m}$ can be calculated for two series of solutions with constant but different salt concentrations and uniformly increasing contents of the solvating solvent:

$$\bar{m} = \frac{c''_{\text{Solv}} - c'_{\text{Solv}}}{c''_A - c'_A}, \tag{17}$$

where c''_A and c'_A, on the one hand, and c''_{Solv} and c'_{Solv}, on the other, are the overall concentrations of the components in two solutions belonging to two different series. In order to evaluate the formation constants, one calculates initially the equilibrium concentration of the solvating solvent:

$$[\text{Solv}] = \frac{c''_A c'_{\text{Solv}} - c'_A c''_{\text{Solv}}}{c''_A - c'_A}, \tag{18}$$

and then one plots the relation

$$m = f(\lg[\text{Solv}]). \tag{18a}$$

By studying the electronic spectra, one can follow the formation of complexes with different solvation numbers (up to the maximum value) and one can observe also the variation of the actual geometry of the solvato-complex. The vibrational spectra (infrared and Raman spectra) can be used to investigate solvation, like the electronic spectra. Compared with the pure solvent, the infrared spectra of solvato-complexes show new bands corresponding to the stretching and deformation vibrations of the bonds and reveal shifts of the vibrational wavenumbers and changes in the intensities of certain absorption bands of the solvating solvent. Since solvates dissociate in solution, the measured vibrational spectra show absorption bands referring both to the complex itself and to free solvent molecules. With increase of solvate concentration, the intensity of the former increases and that of the latter falls. In order to determine the composition of solvates, the vibrational spectroscopic results can therefore be treated similarly to electronic spectra. For example, the addition of one ethyl oxalate and one ethyl malonate molecule to $SnCl_4$ was demonstrated by the change in intensity of the stretching vibration band of the bound and free C=O groups in a benzene solution[152].

In a study of the infrared spectra of acetone solutions of MI and $MClO_4$ (M = Li or Na), it was noted that the C=O stretching vibration band shifts towards lower wavenumbers by 3 cm^{-1} for Na^+ and by 8 cm^{-1} for Li^+.[191] Since this shift is independent of the nature of the anion, it was natural to conclude that the cations are solvated much more intensely than the anions[192] and that the capacity for solvation increases from Na^+ to Li^+.

Conductimetric[153] and cryoscopic[154-163] measurements are sometimes used in the study of salt solvates. Thus the solvation of Al_2Br_6 by acetone and nitrobenzene leads to the formation of two compounds: $AlBr_3$.Solv and $AlBr_3$.2Solv.[164] The decrease of the conductivity of an ethereal solution of $AlCl_3$ with increase of the chloride concentration[31] can be accounted for by the conversion of the more complicated partly dissociated solvato-complex into the less complicated compound $[Cl_3Al.O(C_2H_5)_2]$, which agrees with the literature[165,166].

When cryoscopic measurements are used, it is first necessary to determine the association factor of the solvating solvent:

$$F_c = \frac{\Delta t}{\Delta t'}, \tag{19}$$

where $\Delta t'$ and Δt are the freezing point depressions of the solutions found experimentally and calculated theoretically. It is convenient to use dioxan, in which many solvents are not associated, as the inert solvent[131]. The variation of the freezing point depressions of solutions of the solvating solvent and the test substance in dioxan yields

$$\Delta t_1 = qc_1; \tag{20}$$

$$\Delta t_2 = qc_2, \tag{20a}$$

where c_1 and c_2 are the molar concentrations of the solvating solvent and the solute respectively. When solvato-complexes involving the addition of m solvent molecules are formed, the overall freezing point depression is

$$\Delta t = q(c_1 - mc_2 + c_2), \tag{21}$$

whence

$$m = \frac{qc_1 + qc_2 - \Delta t}{qc_2}. \tag{22}$$

The addition of one $POCl_3$ molecule to $FeCl_3$ and $AlCl_3$ in nitrobenzene[167] has been demonstrated cryoscopically.

A frequently used method for the determination of solvation numbers is that of Stokes. By following the movement of the solvated ion in an external electric field, it is possible to calculate the radius of the solvato-complex as follows:

$$r = \frac{0.82z}{\eta\lambda}, \tag{23}$$

where z is the absolute charge of the ion, λ the limiting equivalent conductance of the solution, η the viscosity of the solvent.

In order to find a more accurate value of the radius of the solvated ion, the following equation has been proposed[168]:

$$r' = \frac{0.82z}{\eta\lambda} \cdot \frac{r_{cr}}{r}, \tag{24}$$

where r' is the exact radius of the solvato-complex and r_{cr} the crystal-chemical radius of the ion investigated.

Table 2 shows that the radii of the solvated ions calculated by Eqn. (24) are higher than the Stokes values. Furthermore, according to Della Monica and Senatore[169], the solvation of cations should take place more vigorously than that of anions, since the radii of the solvato-complexes of the latter are smaller.

The volume of the solvation shell can be found from the radii of the solvated ions by means of the equation

$$V_{Solv} = \frac{4}{3}\pi(r^3 - r^3_{cr}), \tag{25}$$

and then the solvation number can be obtained:

$$m = \frac{V_{Solv}}{V}, \tag{26}$$

where V is the volume of one solvent molecule. Calculation based on Eqns. (24)–(26) led to the determination of the solvation numbers of Li^+: 4.6 (in water); 5 (in acetone); 6 (in acetonitrile); 11 (in ethanol). We believe these values to be too high.

Table 2. The radii r and r' (Å) of certain solvated ions in a number of solvents calculated by Eqns. (23) and (24).[169]

Ion	Methanol		Acetonitrile		DMF		Sulpholane		Nitrobenzene		Formamide	
	r	r'	r	r'	r	r'	r	r'	r	r'	r	r'
Li^+	3.77	4.74	2.98	4.13	4.12	5.10	1.92	3.74	—	—	2.92	4.36
Na^+	3.32	4.46	3.10	4.24	3.45	4.46	2.30	4.23	2.78	3.99	2.46	3.99
Cs^+	2.40	3.88	2.44	3.68	2.99	4.04	1.95	3.78	—	—	1.84	3.48
Cl^-	2.86	4.16	2.54	3.76	1.87	3.00	0.89	1.98	2.04	3.32	1.45	3.14
I^-	2.39	3.88	2.38	3.56	1.97	3.09	1.15	2.47	2.22	3.49	1.45	3.21
NO_3^-	2.80	4.14	2.24	3.48	1.80	2.92	—	—	2.00	3.30	1.44	3.14

In order to investigate ion solvation, a potentiometric method was proposed in 1958[92,93,95] whereby it is possible to deduce the existence of both homogeneous and mixed solvato-complexes. As in the usual complex-forming systems[170-172], the inert solvent should possess some ionising capacity and the metal corresponding to the salt should form an effective electrode of the first kind. If the solvating solvent binds metal ions into solvates more effectively than the inert solvent, its introduction into the system leads to a decrease of the electrode potential. Knowing the overall concentration of metal ions c_M and having determined its equilibrium value [M] potentiometrically, it is possible to calculate the solvation number of the ion:

$$m = \frac{d \lg \frac{c_M - [M]}{[M]}}{d \lg [Solv]}, \tag{27}$$

where [Solv] is the concentration of the solvating solvent. The formation constant of the solvato-complex can be calculated from Eqn. (16), having assumed that $[A.m\,Solv] = c_M - [M]$ and having replaced [A] by [M].

A combined graphical and analytical treatment of the potentiometric data[95,172] established that the hydration of lead and silver ions changes by 3–4 coordination sites as high concentrations of dioxan and acetone are reduced in the presence of water[93,170]. This is due to the formation of mixed solvates. Homogeneous hydrates of lead ions $[Pb(H_2O)_6]^{2+}$ are detected at high water concentrations in the $Pb(ClO_4)_2$–CH_3OH–H_2O system[173] and the solvates $[M(DMF)_6]$ are detected[174] in the $M(ClO_4)_n$–DMF–H_2O systems, where M = Cd, In, or Sn.

The formation of solvato-complexes can be observed also in a direct study of the properties of solvent molecules. This is achieved best with the aid of the NMR method[175-177] using the chemical shift δ. When the experiments are performed at a fixed frequency $\nu_{av} \simeq \nu_0$, the distance between the signals of the test and standard solutions being determined, the chemical shifts can be estimated as follows:

$$\delta_i = \frac{\nu_i - \nu_{av}}{\nu_{av}} = \frac{\nu_i - \nu_{i\,av}}{\nu_0}. \tag{28}$$

If the solvent molecules with resonating nuclei are attached to a solute molecule or ion, the chemical shift of the nuclei is displaced relative to that of the free solvent molecules. In the absence of exchange between the solvato-complex and free molecules or when its rate is low, the NMR spectrum shows lines due to the resonance of the nuclei of the coordinated and free solvent molecules. By measuring the integral signal intensities, it is possible to determine the concentrations of the bound and free solvent and to calculate from the known concentration of the solute the solvation number and the equilibrium constant for the formation of the solvato-complex[175-188]. In particular, the solvation number can be calculated[184,185] with the aid of the equation

$$m = i\frac{S_c}{S_c + S_f}, \tag{29}$$

where i is the total number of moles of the solvent per mole of the solute and S_c and S_f are the areas under the signals due to the bound and free solvent. Using Eqn. (29), Yatsimirskii et al.[186] found that five water molecules are retained by Lu^{3+} in an acetone solution of $Lu(NO_3)_3.6H_2O$. However, the overall coordination number of lutetium reaches at least 8, since the conductivity of the test solution at a concentration of 0.01 M is extremely low.

On the other hand, when there is an appreciable exchange between the free and bound components of the solvato-complex, the NMR spectrum reveals a single signal:

$$\delta = \delta_1\frac{c_1}{c} + m\frac{c_m}{c}\delta_m, \tag{30}$$

where δ is the average chemical shift of the solvent molecules, δ_1 and δ_m are the chemical shifts of the atoms in the free solvent and the solvent bound in the complex, m is the solvation number, and c_1, c_m, and c are the concentrations of the free solvent, the bound solvent, and the entire active solvent in the system. In particular, the presence of the complexes $[Gd(H_2O)_9]^{3+}$,[182] $[ThCl_4.2DMF]$,[94] and $[Al(DMF)_6]^{3+}$[188] has been established using Eqn. (30). The solvation numbers found for Mg^{2+} are 5 in liquid ammonia[183] and 5 with respect to methanol and 5.7 (with respect to water) in water–methanol mixtures. The authors explained the deviation of the overall solvation number of magnesium from 6 by the partial incorporation of perchlorate ions in the coordination sphere[184]. The more vigorous solvation of Li^+ was established in a study of the NMR spectra of solutions of lithium and sodium salts in DMSO.[187]

In the course of solvation, it is possible to determine the chemical shift of the solvent also in the presence of paramagnetic ions, which influence the NMR spectra as a result of the exciting effect of the unpaired electron on the electronic structure of the solvent molecule. The chemical shift can then be defined as follows:

$$\delta = \frac{8\pi|\psi(0)|^2}{3p}c_{Solv}, \tag{31}$$

where $|\psi(0)|$ is the probability that the unpaired electrons are located near the solvent protons, c_{Solv} the concentration of the solvating solvent in solution, and p a quantity which includes the solvation number of the metal ion. The hexasolvates of nickel and cobalt(II) in acetonitrile have been detected with the aid of Eqn. (31).[189,190]

The X-ray diffraction method is promising for the detection of solvato-complexes. It has been stated[193-196] that there is an analogy between the structures of solids and the corresponding liquid systems. In particular, an octahedral environment has been demonstrated for copper, cobalt, and nickel cations in aqueous solutions[194]. The intensities of X-ray scattering by the solvent and the solution are usually determined by this method and data for the structure of the liquid are obtained by analysing the areas under the maximum of the atomic-electronic density distribution function. The position of the maximum on the distribution curve yields the average distance between the coordinated species. Having measured the area under the maximum on the experimental distribution curve, it is possible to determine the coordination number of the species. Although X-ray diffraction analysis does not always lead to an accurate determination of the bond lengths and valence angles, nevertheless, it has shown that hexasolvate cations are formed in 2–2.5 M $CuCl_2$ and $CoCl_2$ solutions in methanol, ethanol, and dimethylformamide. The chloride ions are then distributed in the secondary solvation shell[136,137].

In order to confirm the conclusions concerning the possible solvates in solution, their preparative study is extremely useful[128,197,198]. As in the physicochemical study of solutions, the synthesis of solvates from different solvents does not by any means always yield the same solvation numbers. This is due to the nature of the solvating solvent and the specific conditions governing the applicability of the research technique.

VI. THE DONOR ACTIVITY OF SOLVENTS

Data concerning the displacement of molecules of one solvent by another in solvato-complexes[92,200-202] can serve as a basis for the estimation of their donor activity. In this respect, valuable information is provided by infrared spectroscopy. For example, the decrease of the solvating capacity of alcohols with respect to Co^{2+} in the following sequence has been demonstrated on the basis of the shift of the absorption band due to the stretching vibrations of the OH group[203]:

$$CH_3CH((OH)CH_3 > (CH_3)_3COH > C_2H_5OH > CH_3(CH_2)_2OH \simeq CH_3(CH_2)_3OH >$$
$$> CH_3CH(OH)C_2H_5 > CH_3(CH_2)_4OH.$$

The solvating capacity of solvents is sometimes estimated from their basicity:

$$H^+ + Solv \rightleftarrows HSolv^+.$$

The higher the constant K_a for the above equilibrium the higher the donor activity of the solvent. Thus the pK_a values for acetone (7.2) and acetonitrile (10.13), which in most cases behave as weakly solvating solvents, are appreciably lower [higher?] than that for dimethyl sulphoxide (0.00).[204]

The sequence of solvent basicities indicated above is consistent with the sequence of solvating capacities determined by other methods. Thus the following sequence in the variation of the donor activities of solvents has been established by NMR from the concentration variation of the chemical shift δ[Eqns. (30) and (31)] of the water protons in water–non-aqueous solvent mixtures in the presence of $AlCl_3$, $TiCl_4$, or $CoCl_2$:[205]

$$DMSO > CH_3OH > C_2H_5OH > [(CH_3)_2N]_2CO \simeq THF > (CH_3)_2CO \simeq CH_3CN \simeq C_4H_8O_2.$$

As was to be expected, the values of δ for the solvating solvent protons are not correlated with their dipole moments and the dielectric constant ϵ.

To compare the abilities of various ions to combine with the same solvent, Izmailov[206] determined their solvation energies assuming them to be similar for isoelectronic ions and assuming that they decrease with increase of the square of the principal quantum number (n^2) of the vacant orbitals. The determination of the solvation energy of the ion reduces to the extrapolation of the almost linear function

$$\Phi = \frac{1}{2}\left[Q_{\text{ion}} + (Q_{\text{Hal}} - Q_{\text{M}^+})\right]. \tag{32}$$

The calculations are performed for $n = 3$, 4, 5, or 6 and Eqn. (32) is then extrapolated to $1/n^2 = 0$. In this case, M^+ is the alkali metal ion. The corresponding sums and differences are determined from the e.m.f.'s of cells with and without transport:

$$\lim \Phi = Q_{\text{ion}} \text{ when } \frac{1}{n^2} \to 0.$$

The values of Q for M^+ and Hal^- in water, ammonia, methanol, and ethanol were calculated from the experimental data. The results of the calculation for the same metal ion lead to the conclusion that the donor activities of the solvents vary.

A comparative assessment of the solvating capacities of the solvents can be made also by comparing the equilibrium constants for the dissolution of substances in mixed solvents evaluated by Eqn. (12). Thus it has been shown for dioxan–solvent mixtures[128,190] that the solvating capacity varies in the following sequence: ethanol < methanol < dimethylformamide.

Table 3 shows that the negative logarithms of the constants for the equilibrium

$$CuCl_2 + 2Solv \rightleftarrows CuCl_2 \cdot 2Solv$$

in dioxan solution increase from dimethylformamide to ethanol. According to the p*K* value, water follows ethanol in this sequence, which appears to show that its solvating activity is weak. This can be accounted for by the ability of dioxan[207] to form strong hydrogen bonds with water. Bearing this in mind, the method under consideration cannot be regarded as universal for the estimation of the donor activities of solvents. The method based on the comparison of the formation constants of solvates calculated by Eqn. (16) and other methods involving the use of an inert solvent suffer from the same disadvantage.

Table 3. The negative logarithms of the formation constants of the solvates $MCl_5.2Solv$ in dioxan solutions.

Solvent	ε	p*K*		
		$CuCl_2$	$CdCl_2$	$NiCl_2$
Methanol	32.6	2.30	3.67	2.62
Ethanol	24.3	2.36	3.75	2.72
Dimethylformamide	36.1	1.44	3.58	2.51
Water	81	2.89	4,36	—

Depending on the donor activity of the solvent, the heat of the solvation reaction

$$A + m\text{Solv} = A \cdot m\text{Solv} + \Delta H$$

will be different. Makarova and Pominov demonstrated in this way the different solvating capacities of alcohols, acetone, and acetonitrile in relation to $CoCl_2$.[208] However, here too one cannot estimate the absolute solvent activities. For this reason, Lindquist and Zackrisson[209] suggested that the donor capacity be determined relative to a standard acceptor ($SbCl_5$ or $SnCl_4$) with which the given donor is combined in 1 : 1 proportions (this should entail the same entropy change). The authors established calorimetrically the following series of solvents based on their decreasing donor capacities:

$$(CH_3O)_3PO > (CH_3)_2SO > (CH_3)_2CO > POCl_3 > SOCl_2.$$

Gutmann and Wychera used the same considerations and introduced the concept of the donor number, which is understood as the numerical value of the enthalpy of addition of a solvent molecule to a molecule of antimony pentachloride in dichloroethane[210]:

$$DN_{SbCl_5} = -\Delta H_{Solv.SbCl_5}. \tag{33}$$

Table 4 shows that the dielectric constant and the donor number of the solvent do not vary in parallel. This shows that the covalent interaction predominates over the electrostatic interaction in solvation processes.

Table 4. The donor numbers and the dielectric constants of certain solvents[51].

Solvent	ε	DN_{SbCl_5}	Solvent	ε	DN_{SbCl_5}
1,2-Dichloroethane	10.1	—	Ethyl ether	4.3	19.2
Nitromethane	35.9	2.7	Tetrahydrofuran	7.6	20.0
Acetonitrile	38.0	14.1	Tributyl phosphate	6.8	23.6
Tetramethylene sulphone (sulpholane)	42.0	14.8	Dimethylformamide	36.1	26.6
Acetone	20.7	17.0	Dimethyl sulphoxide	45.0	29.8
Ethyl acetate	6.0	17.1	Pyridine	12.3	33.1
Water	81	18	Hexamethylphosphoramide	30.0	38.8

A calorimetric study of the solvation of ECl_4, where E = Zr or Hf, in nitromethane established[211] the following series based on the donor activities of solvents:

$$(CH_3)_2SO > (CH_3)_2NCOH > CH_3CN > CH_3NO_2,$$

It agrees with the data in Table 4.

Nevertheless, the same solvent can manifest different solvating capacities with respect to different solutes. Because of this, the solvating capacities of solvents cannot be treated as non-relative quantities and Gutmann's donor numbers cannot be treated as absolute solvent characteristics. For example, acetonitrile does not possess a high capacity for the formation of compounds with Na^+, Pb^{2+}, and Ca^{2+} ions, but it forms solvato-complexes with $AlCl_3$, $GaBr_3$, BF_3, $SnCl_4$, and $TiBr_4$ (without substituting halide ions).[87]

In contrast to the available donor numbers of acetone, ethyl ether, and other ethers (Table 4), the energy of solvation of $NbCl_5$ by acetonitrile (−37.8 kcal) is much higher than the energy of solvation by ethyl and butyl ethers (−21.0 kcal), dioxan, and esters[212]. These findings suggest that the donor activities of solvents are determined not only by their individual properties but also by the specific features of their interaction with the solute.

For a more objective determination of the donor activities of solvents, one can isolate the solvates and determine thermochemically the solvation energies[128,130]. Such a calculation can be performed in connection with the determination of the integral heats of solution of the solvate (ΔH_3), the substance in the absence of the solvating solvent (ΔH_2), and the corresponding solvents (ΔH_1) in water or another liquid in which all the substances enumerated dissolve. The solvation energy can be calculated from the equation

$$\Delta H = \Delta H_1 + m\Delta H_2 - \Delta H_3. \tag{34}$$

Table 5 shows that the solvating capacity of dimethylformamide is highest, water occupying the second place as regards donor activity. The value of the hydration energy obtained for $CuCl_2.2Solv$ is somewhat difficult to understand[130].

Table 5. The solvation energies (kcal) of certain metal chlorides.

Solvent	$CuCl_2\cdot 2Solv$	$CaCl_2\cdot 2Solv$	$ZnCl_2\cdot 2Solv$	$NiCl_2\cdot 2Solv$
Methanol	7.41	4.16	8.20	5.68
Ethanol	7.32	4.49	—	5.62
Dimethylformamide	10.32	7.14	13.13	9.78
Water	7.20	6.10	—	8.47

VII. COMPLEX FORMATION REACTIONS IN NON-AQUEOUS AND MIXED SOLUTIONS

In contrast to aqueous solutions, in the interaction of ions in non-aqueous solutions a multiplicity of anomalies are observed. In the presence of water, the stability of the halides of $s^2p^6d^{10}$ and $s^2p^6d^{10}s^2$ cations decreases in the sequence $I^- > Br^- > Cl^-$. On the other hand, according to a number of workers[213-215], the variation of the conductivities of halides in pyridine solutions follows the opposite sequence. However, if one employs a series of salts with the same anion, then their conductivities in pyridine decrease in the sequence

$$Ag^+ > Li^+ > K^+ > Na^+,$$

i.e. in conformity with the ability of the cations to form pyridine complexes. Only the position of potassium in this series is somewhat incomprehensible, since K^+ is usually less solvated than Na^+. Since potassium ions form relatively unstable solvato-complexes with pyridine, the interaction of $AgNO_3$ with KSCN and even with K_2HgI_4 in this solvent takes place only in consequence of the precipitation of KNO_3.[40,41]

The role of non-aqueous solutions in complex-formation processes involving readily hydrolysed ions is especially great. In particular, the study of the majority of metal selenocyanates involves considerable difficulties. The $\mathrm{C}\overline{\cdots}\mathrm{Se}$ bond in the selenocyanate ion $\mathrm{N}\overline{\overline{\cdots}}\mathrm{C}\overline{\cdots}\mathrm{Se}^-$ is weak and the ion therefore decomposes with elimination of selenium both under the influence of light and in an acid medium. It is quite reasonable that $NCSe^-$ should be stabilised when the electron density of selenium is increased, i.e. when the selenocyanate ligand is bound to a central atom with an enhanced π-donor capacity. Mainly $s^2p^6d^{10}$ ions in the Fifth and Sixth Periods of the Periodic System possess this property. This is why it is possible to detect in aqueous solutions the selenocyanate complexes of silver, mercury, cadmium, gold and one or two more metals with electronic structures similar to that indicated above. On the other hand, La^{3+}, Cr^{3+}, V^{3+}, Mn^{2+}, Zr^{4+}, etc. exhibit only a weak capacity for the formation of dative bonds and, in contrast to the metals listed above, form only unstable E–NCSe linkages, which cannot compete with the $E-OH_2$ or E–OH linkages arising in consequence of hydrolysis. A decrease of pH results in the decomposition of the selenocyanate ligand in such systems and the efficiency of the formation of transition metal selenocyanates can therefore be increased only in non-aqueous solutions[216,217]. Similar effects occur in the study of complex-formation reactions between polyvalent cations and nitrite ions and other weak acid anions[218].

Interesting data have been obtained for the influence of solvents on the complex-formation reaction[61] when silver halides are dissolved in the presence of $AgNO_3$ and $AgClO_4$.[103] The Ag_3I^{2+} dissociation constant varies as a function of the nature of the solvent in the following way:

$(CH_3)_2CO$	H_2O	$(CH_3)_2SO$	CH_3CN
10^{-19}	$10^{-14,1}$	$10^{-10,8}$	10^{-10}

It is seen from these results that dimethyl sulphoxide, in its role as an active solvating agent (with a donor number of 29.8), promotes to a greater extent than water the dissociation of the complex, while acetone tends to stabilise it, although the donor number of acetone is close to that of water (Table 4). On the other hand, acetonitrile has a much lower donor capacity (a donor number of 14.1) and the stability of the complex Ag_3I^{2+} in this solvent is lower than in other solvents. Similar facts have been quoted by Surpina et al.,[219] who noted that in acetonitrile the interaction of $NbCl_5$ with azoles and Schiff bases proceeds with greater difficulty than in esters. This demonstrates yet again that Gutmann's donor numbers are relative[51].

Like dissolution, complex formation depends wholly on the solvation of the central ion and the ligands. The greater the strength of their bonds with solvent molecules, the more difficult it is to make them come together. On the other hand, if the solvent molecules can be removed from the solvato-complexes by binding them to another solvent, then an interionic linkage is formed more readily. This is why it has been possible to detect in aqueous dioxan solution the complex $[Cd(SCN)_6]^{4-}$, which is not formed in water, other conditions being equal[95]. The study of complex-forming systems in mixed and purely non-aqueous solutions permits the formulation of the rule governing the composition of the complexes: the addition to an aqueous solution of a donor-active solvent at moderate and high concentrations of the latter permits the formation of complicated complexes, but, following the attainment of a concentration of 90—100%, the number of acido-ligands in the coordination sphere falls again[95,173,220]. This rule operates in the study of not unduly stable complexes and can be explained by the fact that, at moderate concentrations of the non-aqueous solvent, the latter binds water and facilitates the incorporation of acido-ligands in the coordination sphere in place of water. When its concentration is higher, the non-aqueous solvent itself combines with the central atom and prevents the addition of other ligands.

As a result of the formation of stable dioxan–water compounds[205,220], the activity of water falls and lead–antimony alloys cease to be corroded in the mixed solvent[29]. An increased solvation effect prevents the formation of nickel and cobalt hexaselenocyanate and even tetraselenocyanate complexes in pure dimethylformamide[221], of anionic copper(II) complexes in dimethyl sulphoxide[222], and of molybdenum(V) complexes in hexamethylphosphoramide[223]. Tin forms only $[Sn(NCS)_3]^-$ in dimethylformamide, while the complex in methanol and acetonitrile is $[Sn(NCS)_4]^{2-}$.[174,224] On the other hand, cadmium combines with four thiocyanate ligand species in methanol and dimethylformamide and with six such species in acetonitrile. The stability of cadmium, indium, and tin thiocyanate complexes increases on passing from dimethylformamide to acetonitrile via methanol[225,226].

The examples examined above show that, contrary to the conclusion reached in the literature[227,228], the chemical nature of the solvent has a greater influence on complex formation than the dielectric constant. In solvents which form stable solvates with metal ions, the combination of these ions with other ligands proceeds with greater difficulty. In acetonitrile, $ZnCl_2$ behaves as a stable complex because Zn^{2+} is only weakly solvated by the molecules of this solvent. As a result, the variation of the zinc electrode potential with the concentration of such a solution is anomalous[30]. In acetonitrile, zinc forms anionic chloro-complexes more readily than highly solvated mercury(II). $HgCl_2$, which forms stable solvato-complexes is converted into $[HgCl_4]^{2-}$ in acetonitrile with greater difficulty than in water[229], although the donor number of water is higher[51].

Depending on the nature of the solvent, the sequence of ligands in the series based on the stability of the given metal complexes can also change. For example, the stability of cadmium and lead halide complexes in alcohols and water increases from the chlorides to the iodides, while in dimethylformamide the variation is in the opposite sequence[230-233]. The inversion of the stability sequence of lead halides can be readily accounted for by the enhancement of the solvation of the anions by dimethylformamide and by the increase of their radii. That this is indeed so can be seen from the fact that NaI dissolves more readily in dimethylformamide (and formamide) than NaCl. Furthermore, the enthalpies of solution of metal halides in DMSO vary in the sequence[234]

$$Cl^- > Br^- > I^-.$$

The study of mercury(II) halides in DMF[235], DMSO[236], and dimethylacetamide (DMA)[237], which have very similar donor numbers, has revealed an appreciable variation of the stabilities of these complexes in the following sequence of solvents:

$$DMSO < DMF < DMA < H_2O.$$

The explanation of the dependence of the complex formation reaction on the nature of the solvent taking into account solvation has been confirmed in numerous experiments[220-226,238-244]. The electronic absorption spectrum of the $Co(ClO_4)_2$–NaNCSe–DMF solution with a monomolecular or bimolecular proportion of selenocyanate has a band at 525 nm, i.e. in the region corresponding to the absorption by the octahedral complexes $[Co(NCSe)(DMF)_5]^+$ formed (only the optical density increases). On the other hand, in the presence of a large excess of $NCSe^-$, a new band appears at 625 nm,[243] which is due to the tetrahedral complex $[Co(NCSe)_4]^{2-}$.

In choosing a solvent promoting complex formation, one must take into account both its solvent power with respect to the reactants and the nature of its interaction with the complex formed. The most marked effect of complex formation can be achieved when the donor activity of the solvent is low. For example, in acetone mercury(II) nitrate behaves as a stable complex[242]. Whereas, in acetone, acetonitrile, and other similar solvents Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and In^{3+} ions form readily hexa- and tetra-halogeno- and hexa- and tetrathiocyanato-complexes, in dimethylformamide and dimethyl sulphoxide complexes with low coordination numbers are formed even in the presence of an excess of acido-ligand[221,224,244]. In DMSO, even the proton is very strongly bound[245].

The study of the Raman laser spectra and the freezing points of the solutions showed that, depending on the concentration, phosphorus pentachloride forms the following complexes in acetonitrile, nitromethane and nitrobenzene:

$$2PCl_5 \rightleftarrows [PCl_4]^+ + [PCl_6]^- \qquad (> 0.03\ M)$$

or

$$PCl_5 \rightleftarrows [PCl_4]^+ + Cl^-. \qquad (< 0.03\ M).$$

On the other hand, in solvents such as benzene and carbon tetrachloride, it behaves as the neutral complex $[PCl_5]$.[246]

By selecting solvents in accordance with the above relations, it is possible to detect in non-aqueous solutions numerous complexes which are not formed in aqueous solutions.

VIII. THE INFLUENCE OF SUPPORTING ELECTROLYTE IONS AND "STEPWISE" COMPLEX FORMATION

In many non-aqueous solutions, the initial electrolytes exist as ion pairs, but it is nevertheless possible to demonstrate in such solutions the formation of complexes with substances capable of forming strong bonds with the ions of the given electrolyte. The composition of the complexes in such systems can be readily determined by physicochemical methods and it is even possible to calculate conventional equilibrium constants for the complex-formation reactions. However, depending on the nature of the initial salt of the given metal, the equilibrium constants are not the same in the particular solvent. Thus, the formation of the complex $[Co(NCSe)_4]^{2-}$ with a conventional equilibrium constant of 7.0×10^{-14} was established in the $Co(ClO_4)_2$–NaNCSe–$(CH_3)_2CO$ system[240], while in the presence of cobalt nitrate the equilibrium constant for the same complex proved to be higher.

On the other hand, if the initial salt includes anions which can be bound strongly to the given cation, then the determination of the composition of the complexes yields a low number of ligand species incorporated. This can be explained by the formation of mixed complexes. In particular, a study of the $MoOCl_3$–NaNCSe–$(CH_3)_2CO$ system established the existence of the complex $[MoOCl_3(NCSe)]^{2-}$, which is then converted into $[MoOCl_2(NCSe)_3]^{2-}$ and $[MoOCl(NCSe)_4]^{2-}$.[247]

The formation of a large number of mixed complexes in both aqueous[248] and non-aqueous[245-253] solutions has now been demonstrated. In many instances, mixed complexes are formed more readily than homogeneous complexes. This is apparently due to an energy gain in consequence of the formation of an asymmetric structure, as happens in platinum complexes in accordance with the *trans*-influence principle[254]. When mixed complexes are formed, both the mutual influence of the ligands and the nature of the solvent play an extremely significant role. It is appropriate to note here that the $O(C_2H_5)_2$ molecule combines with BF_3 more readily than the fluoride ion[256,257] in consequence of "chemical symbiosis".[255]

Attempts are sometimes made to explain why mixed complexes are favoured by thermodynamic factors on the basis of the concept of hard and soft acids and bases[13]. In terms of Pearson's rule, the bonds formed by Be^{2+} and

Al^{3+} with acetate ions as well as those formed by the proton with OH^- and F^- should be regarded as ionic, the hydride ion should readily combine with Hg^{2+}, and the Cl^- ion in complexes should behave like the fluoride ion.

In reality this is not so. The formation of hydrides is not characteristic of silver, gold, and mercury. The chloride ion behaves similarly to bromide, iodide, and even thiocyanate. This is why there is a possibility of their mutual substitution with formation of mixed complexes[248,258,259].

For example, the formation of mixed complexes of the type $[E(NCS)_2Cl_2(Solv)_2]$ by zirconium and hafnium can be demonstrated by conductimetric study of the ECl_4–NaNCS–CH_3CN system[260] and $[E(OH)_2(NCS)_2(Solv)_2]$ can be detected when $E(OH)_2Cl_2.7H_2O$ is ground with NH_4NCS in the presence of tributyl phosphate or cyclohexanone[261]. The fact that these are coordination compounds is confirmed by infrared spectra.

If no account is taken of the formation of mixed complexes, then the result of physicochemical study of the corresponding system might lead to the conclusion that the simplest complexes are produced. In reality coordination saturation always takes place in solution owing to the formation of mixed complexes.

The view that complex formation takes place in steps has been firmly established in the literature[135,262-266]. The appearance of each new complex is attributed solely to the kinetic factor, i.e. to the displacement of the equilibrium caused by the increase of ligand concentration. However, this approach is valid only for relatively unstable complexes and provided that account is taken of the incorporation of solvent molecules in the coordination sphere when the E–L and E–Solv bond energies are similar. On the other hand, if $Q(E\text{-}L) \gg Q(E\text{-}Solv)$, then homogeneous complexes EL_n with $n \gg 1$ may be formed even at low ligand concentrations. Under these conditions, only complexes corresponding to the greatest decrease of Gibbs free energy are as a rule produced. Consequently, the thermodynamic and not the kinetic factor is more significant in the formation of stable complexes. Thus when Cu^{2+} interacts with ammonia, the first four NH_3 molecules are bound to the central atom equally strongly, while the fifth molecule combines less effectively[135]. This fact is satisfactorily accounted for by the Jahn–Teller theorem.

Bearing in mind that the incorporation of new ligand species in the complex results in its rearrangement, strengthening some and weakening other bonds, the breakdown of a rigorous sequence based on the increase in the number of species in the complexes with increasing concentration of the corresponding ligand, is quite reasonable. This is why Bjerrum's method has frequently proved unsuitable in the study of non-aqueous solutions[135]. In its general form, this method appears to give a positive result and the relation defined by Eqn. (18a), in which [Solv] has been replaced by the concentration of the acido-ligand, is smooth with distinct horizontal plateaux indicating a high probability of individual complexes. For example, only complexes with $m = 2$, 4, or 6 have been clearly detected in the $E(ClO_4)_2$–NaNCSe–CH_3OH systems, where E = Co or Ni.

It is very remarkable that in methanol, where the stability of nickel selenocyanate complexes is low, the formation function varies more uniformly than in acetone[243]. The formation curve for the cobalt complex reveals the presence of steps also in methanol for $NCSe^- : Co^{2+} = 2$, 4, and 6.[240] More distinct inflections occur in the curve for the acetone solutions, where the stability of the complex is higher.

In contrast to the dimethylformamide solution, an intense band at 400 nm and a weak band at 630 nm appear in the spectrum of the acetonitrile solution already for $Co^{2+} : NCSe^- = 1 : 1$.[243] Bjerrum's formation curve clearly reveals only two steps with $\bar{n} = 1$ and $\bar{n} = 4$. Palladium coordination numbers of 4 and 2 are most clearly manifested in the $PdCl_2$–NaNCSe–DMF system. The latter corresponds to the mixed complex $[PdCl_2(SeCN)_2]^{2-}$.[267]

The formation of only HgI_2 and $[HgI_4]^{2-}$, which are thermodynamically more stable than HgI^+ and HgI_3^-, can be demonstrated in the $Hg(ClO_4)_2$–NaI–solvent systems, where the solvent is an alcohol, acetonitrile, etc.

In dimethyl sulphoxide, Fe^{3+} ions react with CN^- to form only $Fe(CN)_2^+$, $Fe(CN)_3$, and $Fe(CN)_4^-$, or, more precisely, mixed complexes, while the reaction with the fluoride ion yields $[FeF_4(DMSO)_2]^-$.[268] It is of interest that in such cases there are no complexes with six acido-ligands. On the other hand, cobalt chloride forms two complexes in dimethylacetamide: $[CoCl(DMA)_5]^+$ and $[CoCl_3(DMA)_3]^-$.[269]

A series of complexes up to $[E(NCS)_8]^{4-}$ were detected in a study of ECl_4–KNCS systems in acetonitrile and dimethylformamide by Bjerrum's method[260], but they are not all equally probable. This is why the presence of $E(NCS)_4$ is established in experiments involving isomolar series of solutions in dimethylformamide, while $[E(NCS)_6]^{2-}$ is found in acetonitrile. The higher solvating capacity of dimethylformamide under the same conditions leads to the formation of complexes with a smaller number of NCS ligand species than in acetonitrile. It would appear that $E(NCS)_4$ are simple complexes with a coordination number of 4. However, this is not the case, because the complexes $E(NCS)_4.4DMF$, where according to infrared spectra the NCS groups and solvent molecules are coordinated to the metal atom, are isolated from solution[260].

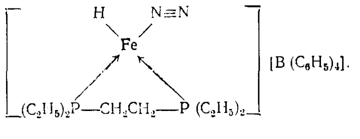
The study of non-aqueous solutions demonstrated the possibility of the coordination of ions which do not usually form complexes in aqueous solutions. In particular, the nitrate ion hardly behaves as a ligand in consequence of its hydration in dilute aqueous solutions. Only at high concentrations of NO_3^- does the potential of the lead electrode decrease[270]. In acetone and even in alcohols, which combine with the nitrate ion less effectively than water, the nitrate ion ceases to be indifferent[44,60]. The coordination compound $[K_2Pb(NO_2)_3(NO_3)]$, in which the nitrate ions behave as a ligand, can be obtained from methanol[271].

Bearing in mind that in many non-aqueous solutions the so called indifferent anions are only slightly dissociated from the corresponding complex-forming agent, in the determination of the compositions of the most involved anionic complexes, one must employ series of solutions with a constant concentration of the initial salt. The study of isomolar series in many instances leads to the determination of the simplest complexes, which are in reality mixed complexes[267,272,273]. The complex $[Pd(SeCN)_4]^{2-}$ has been detected spectrophotometrically in the $PdCl_2$–NaNCSe–DMF system at a constant palladium concentration and variable NaNCSe concentrations, while in the isomolar series of solutions only $[PdCl_2(SeCN)_2]^{2-}$ was detected[267]. Similar results have been obtained also for thorium thiocyanate[273].

Valuable information can be obtained by studying complex formation using the solubility method. In contrast to other methods, the application of which requires a constant concentration of the central atom, in this case both the concentration of the ligand and of the central atom is varied from mixture to mixture. This is why in systems where the ligand and the central atom are capable of forming strong bonds, the solubility method leads to the detection of complexes with a lower component ratio than other methods. This rule[220,274,275] has been confirmed in a large number of experiments[274-283]. While the anionic complexes $[Pb(XCN)_6]^{4-}$ have been detected potentiometrically in methanol[274,282], only the complexes $[Pb(XCN)_4]^{2-}$, where X = S or Se, have been detected by the solubility method and in acetone only the complexes $[Pb(XCN)_3]^-$ have been found[277,283]. In aqueous acetone solution with an acetone concentration of 7 M, the complex $[Ag(SCN)_4]^{3-}$ has been detected potentiometrically at a constant silver concentration, while, according to the results obtained by the solubility method, the complex $[Ag(SCN)_2]^-$ predominates in acetone[277]. Copper[279], silver[280], palladium[267], mercury(II),[281] and lead[282-284] iodides and selenocyanates behave similarly.

IX. NON-AQUEOUS SOLUTIONS IN PREPARATIVE INORGANIC CHEMISTRY

The use of non-aqueous solutions has greatly extended the scope of inorganic synthesis in the field of organometallic compounds[285-287], metal polycarbonyls and their derivatives[288], metal and semimetal hydrides[289-291], salt-like inorganic compounds which are extremely sensitive to water and atmospheric oxygen[292,293], boron compounds with organic ligands[294], and coordination compounds of transition metals with molecular nitrogen[295-297] and carbon dioxide[298]. For example, the iron compound[294]



has been obtained in acetone.

The reaction of cyclopentadiene with metallic potassium in benzene was discovered as early as the beginning of the present century[285]. On the other hand, NaC_5H_5 was not obtained until 50 years later in DMF, THF and 1,2-dimethoxyethane. The so called sandwich compounds of transition metals were synthesised by exchange reactions between NaC_5H_5 and metal halides in tetrahydrofuran or other similar solvents[300] and then also mixed compounds, for example $C_5H_5Fe(CO)_3$.[301] The reactions of metal polycarbonyls with halides[302], isonitriles[291,300], amines, and cyanides[303,304] made it possible to obtain many mixed coordination compounds.

Since several reviews have been devoted to the problem of the synthesis of the above and other compounds, one need consider only the general characteristics of the preparation and crystallisation of coordination compounds from non-aqueous media taking into account solvation effects. In particular, diborane reacts with LiH to form $LiBH_4$ only because the lithium ion can be solvated by ethyl ether, but there is no interaction between diborane and NaH.[305]

Interesting data have been obtained for the synthesis of coordination compounds from boranes[306-308]. Thus diborane reacts with sodium amalgam in ether to form the triboranide NaB_3H_8 (together with sodium tetrahydroborate), while tetraborane reacts with ammonia to give $[(NH_3)_2BH_2][B_3H_8]$ and $[H_3NB_3H_7]$,[306] and with $(C_6H_5)_3P$ to give $[(C_6H_5)_3PB_3H_7]$. Solvents with a higher donor activity than ether decompose the triborane skeleton[308,309].

Another no less important factor concerns the structure of the solvents in which the synthesis is carried out. While the dissolution of salts in water reduces initially to the formation of the hydrates of cations and anions within the limits of the water structure, the majority of even dilute non-aqueous systems consist of combinations of mixed solvato-complexes, where the immediate environment of the cation consists not only of solvent molecules, but also of salt anions behaving as ligands.

At a high concentration of the non-aqueous solution, its structure approaches increasingly that of the corresponding solvate or the pure solute, depending on the solvating properties of the solvent. If in the given solution solvent molecules are not bound very strongly to salt ions, the introduction of another solvent having the same solvating capacity but forming hydrogen or dipolar bonds with the first solvent can lead to the formation of salt crystals without solvent molecules. This is very important for the synthesis of anhydrous salts such as nitrates, perchlorates and others, the hydrates of which undergo hydrolytic decomposition on heating.

When salt solutions in solvents with a high donor activity (DMSO, DMF, etc.) are concentrated, the formation of crystalline structures is preceded by the appearance of comparatively weak forces in the interaction between anions and the molecules of the solvate environment or by electrostatic attraction to the solvated cation. Solvates with a comparatively large (in the case of weakly coordinated anions) or small (if the anions give rise to fairly stable coordinate bonds) content of solvent molecules should be formed from such a solution. For example, copper, cobalt, zinc, aluminium, gallium, indium and many other metal nitrates and perchlorates crystallise in the form of the complexes $MB_n.6Solv$, e.g. $Al(ClO_4)_3.$ $.6DMF$,[188] while the halides, thiocyanates, and selenocyanates of these metals form crystals of $MB_2.4Solv$[221,224] and $ML_3.3Solv$ and $CuCl_2.2Solv$.[222] Solvates of this type are produced from a solvent with a lower donor activity also by nitrates and even perchlorates: $Zn(NO_3)_2.2CH_3CN$, $Sn(ClO_4)_2.2CH_3CN$, $Ni(NO_3)_2.2CH_3CN$,[311] and $Ni(ClO_4)_2.$ $.2CH_3CN$.[312]

In contrast to the perchlorates, an increase of the concentration of the solution leads in the case of halides, thiocyanates, and selenocyanates to a more appreciable substitution of solvent molecules in the solvation shell of the cation by the anions. Such mutual ordering of the ions and solvent molecules with increase of concentration is completed by the separation from the solution of solvates with a reduced content of the solvent, for example: $CdCl_2.2(CH_3)_2CO$,[313] $InBr_3.3N_2H_4$,[314] $ZnPy_2(NCSe)_2$,[315] $Co(NCS)_2.3N_2H_4$,[316] and $Sn(NCO)_2.2C_4H_8O_2$.[316] If a solvent with a high σ-donor activity hinders crystallisation, then active acido-ligands readily enter into the inner sphere and therefore give rise to crystals with a low content of the solvent: $SbCl_3.CH_3COOH$,[317] $SnBr_4.CH_3COOH$,[318] $In(NCS)_3.0.5CH_3CN$,[225] $Sn(NCS)_2.OP(C_6H_5)_3$,[319] $Ga(NCO)_3.$ $.THF$,[316] and $MoOCl_3.2THF$.[310]

When the anion is strongly bound to the cation, the solvent molecules may be completely displaced by the anions. The crystallisation structure then involves short-range order with participation of desolvated ions, which is observed in the formation of the solid phase in an ethereal solution of HgI_2 or $Hg(OCN)_2$[99] and in a formamide solution of $PbCl_2$.[320] Potassium chloride crystallises from dimethylformamide in the unsolvated form and $MgCl_2$ with four solvent molecules[131]. Consequently, the influence of the solvent, hindering crystallisation, is regulated both by the strength of the bonding between its molecules and ions and by interionic forces. As a rule, by selecting the right solvent, it is easy to synthesise many simple and coordination compounds unstable in the presence of water, for example, selenocyanates[216,217,321-326], cyanates[327-330], and mixed coordination compounds each containing two or more different ligands[327-336].

Since the introduction of a non-aqueous solvent miscible with water weakens hydrolysis, the stability of readily decomposed compounds of certain metals can be appreciably increased even in mixed solutions. The influence of the non-aqueous solvent is more appreciable when the E–L bonding is weaker and hydration of the central ion competes appreciably with it. This is why transition metal and aluminium, gallium, bismuth, etc. isothiocyanates, cyanates, and particularly selenocyanates, which are unstable in water, can be isolated from non-aqueous or even aqueous–non-aqueous systems. The use of non-aqueous solvents in the case of lanthanides makes it possible to prevent the decomposition of the selenocyanate ion. However, the solvation of cations is not then prevented. In order to weaken the influence of the latter and to accelerate the separation of the corresponding compounds, it is useful to employ the chelation effect. In particular the following reactions

$$3\,\mathrm{KNCSe} + \mathrm{RCl_3} = 3\,\mathrm{KCl} + \mathrm{R\,(NCSe)_3},$$

where R = Sc, Y or lanthanides, can be achieved in a series of solvents. However, after the separation of KCl, $R(NCSe)_3$ is virtually impossible to crystallise in view of the high stability of the complex species $[R(Solv)_n]^{3+}$. If 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and diantipyrinylmethane (dant) are introduced into such a solution, compounds of the type $[R(NCSe)_3(bipy)_2]$, $[R(NCSe)(dant)_4](NCSe)_2$, and $[R(NCSe)_3(phen)_3]$ are formed immediately[325-327].

The synthesis of zirconium and hafnium selenocyanates $[E(NCSe)_4(bipy)_2]$ from acetonitrile solutions[321], the thiocyanates $R(NCS)_2Ox.6CH_3OH$ from methanol solutions[334], and the complexes MB_2Ox,[335,336] where B = NO_2^-, NO_3^-, Cl^-, NCS^-, or ClO_4^-, R = lanthanide, Al, or Ga, and Ox is the 8-hydroxyquinoline residue, is based on the same principle.

With cations which form less stable solvato-complexes than lanthanides, it is possible to obtain many selenocyanates and mixed coordination compounds $Cat_n[E(NCX)_mB_l]$, where X = O, S, or Se, B = Br, I or Py, and Cat are univalent cations, even from acetone[326-331], methanol, acetone–dioxan, and aqueous methanol[332] solutions.

When the double decomposition reaction between ECl_n and AgNCO is carried out in methanol and AgCl is separated, then, using the chelation effect, it is possible to obtain $[In(NCO)_3phen]$, $[In(NCO)_3bipy]$, $[In(phen)_3](NCO)_3$,[329] $[E(NCO)_2(phen)_2]$, and $[E(NCO)_2(bipy)_2]$,[332,333] where E = Mn, Co, Ni, Zn, or Cu. When a solution containing large outer-sphere cations is added to a methanol solution of $In(NCO)_3$, the compound $Cat[In(NCO)_4]$ is formed[324]. $K_n[Pb(NCO)_{n+2}]$ and $K_2[Pb(NCO)_2(NCS)_2]$,[337] where n = 1, 2 or 3, can be obtained from dimethylformamide.

When $(C_5H_5)_2ZrCl_2$ was allowed to react with AgNCO, the compound $[(C_5H_5)_2Zr(NCO)_2]_2O$ was obtained from acetone solution, and, when gaseous HNCO was passed into the above solution of dicyclopentadienylzirconium chloride, the compound $[(C_5H_5)_2Zr(NCO)_2]$ was formed[338]. The latter as well as $[(C_5H_5)_2Zr(NCS)_2]$ can be obtained also by double decomposition reactions of $(C_5H_5)_2ZrCl_2$ with AgNCO or AgSCN, but in this case in dichloroethane solution[339]. In the latter case the stabilisation of zirconium cyanates is achieved by sandwich-type chelation. It is remarkable that in acetone HOx reacts with $ThCl_4$ to give only the adducts $ThCl_4.mHOx$, where m = 1, 2, 4 or 6, with different coordination numbers. Infrared spectra failed to reveal the presence of free HOx in these compounds; its addition takes place via the nitrogen atom. On the other hand, when a solution of $Th(NCS)_4$ is prepared in the same solvent and an acetone solution of HOx is added, a compound having a different composition is produced: $[Th(NCS)_n(Ox)_{4-n}].nHOx$.[340]

Depending on the nature of the solvent, the same starting materials interact differently. For example, the reaction of $Ni(NCS)_2$ with $[(C_6H_5)_4P]N(CN)_2$ or $[(C_6H_5)_4As]N(CN)_2$, taken in proportions of 1 : 2, results in the formation of $(Cat)_2\{Ni[N(CN)_2]_2(NCS)_2\}$ in methanol and $(Cat)\{Ni[N(CN)_2]_3\}$ and $(Cat)_2[Ni(NCS)_4]$ in acetone[341].

On the other hand, when $Co[N(CN)_2]_2$ interacts with $[(C_6H_5)_4P]NCS$, $(Cat)_2\{Co[N(CN)_2]_2(NCS)_2\}$ is formed in acetone and $(Cat)_2\{Co[N(CN)_2]\}(NCS)_3$ and tetrathiocyanatocobaltate(II) in methanol[342]. [This should be Ref. 341 (Ed. of Translation.]

The influence of the solvent on the structure of the compounds formed merits special attention[218]. In particular, the same starting materials KNCO and AgNCO form $K[Ag(NCO)_2]$ following their interaction in DMF and potassium difulminatoargentate(I) $K[Ag(CNO)_2]$ after interaction in acetone, i.e. a compound having a different structure[343].

X. CONCLUSION

The present development of industry and the associated reduced amount of fresh water available per member of the population have stimulated attempts to place chemical industry on a non-aqueous basis[344]. The problem of solid-phase reactions, the use of fused salt systems, for example the synthesis of monosilane from $SiCl_4$ and LiH in the KCl–LiCl eutectic mixture[345], and of other solutions to carry out various chemical processes with subsequent regeneration of the solvent is already extremely urgent.

Compared with water, the nature of the chemical reaction[50] and the properties of the various substances[223,239] are radically different in many non-aqueous solvents. Thus the solubilities of silver halides in liquid ammonia, acetonitrile, DMSO, and pyridine are much higher than in water. Solubility determinations[346] have shown that the solvent power in relation to AgCl, AgBr, and AgI decreases in the sequence

$$\mathrm{CH_3CN > (CH_3)_2SO > (CN_3)_2CO > C_2H_5NO_2 > CH_3OH.}$$

It is interesting that this sequence is inconsistent with the variation of the donor numbers of solvents (Table 4). This is very important both for the solution of preparative problems (for example, the synthesis of anhydrous salts[347]) and in connection with the use in homogeneous catalysis of certain compounds insoluble in water.

The donor (acceptor) activity of the solvent is the most important factor (compared with others) determining its influence on the corresponding processes. However, such activity may vary with the nature of the solute. The higher the activity, the greater the difficulty of the interaction of the complex-forming agent with other ligands and the greater the ease of formation of mixed solvato-complexes. In the presence of two different acido-ligands, mixed complexes involving them are usually formed more readily in solvents with a lower donor activity. Consequently, depending on the latter, the composition of the complexes of a given central atom with the same ligands should vary in different ways in different solvents.

The influence of the solvent on oxidation-reduction reactions merits attention. Thus, bromine reacts with hydrogen sulphide with liberation of sulphur in the presence of water and with formation of thiohypobromous acid in chloroform[348]:

$$H_2S + Br_2 \rightleftarrows HBr + HSBr.$$

This is associated with different degrees of solvation and hence dissociation of the corresponding compounds in different solutions (as well as the different behaviour of PCl_5 in acetonitrile, nitromethane, and nitrobenzene on the one hand and in benzene and carbon tetrachloride on the other[246]). The unusual influence of the medium has, in fact, made it possible to obtain many at first sight uncommon coordination compounds, including those with zero and negative degrees of oxidation of the central metal atom[349,350]. In the presence of aluminium chloride, fused bismuth chloride is reduced in accordance with the equation

$$BiCl_3 + 2Bi + 3AlCl_3 = 3Bi[AlCl_4].$$

Bismuth tetrachloroaluminate has a melting point of 253 °C.[351] Gallium(I) and cadmium(I) salts can be obtained similarly.

In view of the enhanced specificity of the reactions when water is replaced by other solvents, many [non-aqueous?] solutions are being increasingly used not only in syntheses but also in titrimetric analysis[352-354]. One is then usually dealing with complex-formation reactions.

The study of complex-formation reactions in non-aqueous solutions has greatly extended the range of these reactions[355-358] and permitted the formulation and to some extent also the solution of a number of new problems. It is therefore extremely important to seek an objective characteristic of the solvent which will make possible a more complete prediction than can be done at present of its solvent power in relation to various substances, its influence on complex-formation reactions, and the possibility of synthesising new compounds.

When account is taken of the σ-donor and π-acceptor activities of solvents and also of the ability of various ligands to be coordinated to the corresponding metal atoms, it is possible to predict the dissolution in a number of liquid multicomponent systems under the usual conditions of many substances, such as, for example, oxides, sulphides, selenides, and even metals, which are usually regarded as absolutely insoluble in water, alcohols, ketones, and similar liquids. This problem is of considerable interest from both theoretical and practical points of view.

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The State of Physicochemical Research on Ferroelectric Films

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The review deals with studies on films of complex oxides with unusual dielectric properties. The principal methods for their preparation are described and studies on thin films of barium titanate and solid solutions based on it are considered in detail: the structures at the atomic and supra-atomic levels, the composition of condensed films, structural defects, properties as a function of structure and composition, etc. Data are presented for other ferroelectric complex oxide films as well as thin ferromagnetic layers. Their possible applications are briefly enumerated.
The bibliography includes 257 references.

CONTENTS

I. INTRODUCTION

The continuous development of engineering requires new materials with specified physicochemical properties. Among the materials supplied by chemical industry to meet the requirements of electronic engineering, substances with unusual electrical and magnetic properties (ferroelectric, piezoelectric, and pyroelectric materials, ferrites, etc.) occupy an important place. In recent years increasing attention has been devoted to a research on films of these materials, which are of both theoretical and practical importance.

The principal advantages of electronic devices containing a thin-layer element is simplicity of the technology of their manufacture, microminiaturisation, rapid action, and reduction of the energy consumed and of the controlling fields. On the other hand, a film constitutes a unique model for the investigation of the nature of spontaneous polarisation, side effects, the influence of structural defects on spontaneous deformation, and lattice dynamics, A thin layer is a convenient object for the investigation of the domain and atomic structures of the ferroelectric material up to the determination of atomic coordinates.

The physicochemical properties of films are determined by their chemical composition and atomic-electronic structure. The composition of thin ferroelectric layers is usually more complex than that of metallic, dielectric, and semiconducting films. In the case of mixed oxides, the system consists of 3, 4, and more components, which significantly complicates the mechanism of structure formation, aggravates the phase and structural non-uniformity of the condensed layers, and gives rise to problem of stoichiometry. As a result of the development of electronic probe methods for the analysis of composition and structure, ways have been outlined for determining the compositions of condensates and for optimising the conditions governing the formation of the crystal structure. The role of defects is being more thoroughly investigated. It has become evident that the imperfection of the structure can obscure the true size effects.

After the discovery of barium titanate as a ferroelectric material in the USSR by Vul and Gol'dman[1] (and independently in the USA and Japan), the science of ferroelectricity began to develop rapidly. The relevant monographs[2-10] cover numerous aspects of ferroelectricity, but, with the exception of comparatively short reviews[11-14], the literature on ferroelectric films contains no systematic accounts of data scattered in journal articles, the number of which has sharply increased in recent years.

This review deals with films of oxide ferroelectric materials, which have been the subject of the vast majority of studies on thin ferroelectric layers. Mixed (binary and ternary) oxides have the advantage over other classes of ferroelectric substances as regards relative structural simplicity and the relative simplicity of the technology required to prepare the relevant devices. Ferroelectric materials of the type of barium titanate (with the perovskite structure) have a particularly simple structure, which makes it possible to interpret their properties on a structural basis, and have found extensive practical applications. The restriction of the scope of the review to a discussion of complex oxide films does not rule out the applicability of the fundamental relations of ferroelectricity in thin layers to other classes of materials exhibiting spontaneous polarisation.

II. METHODS FOR THE PREPARATION OF THE FILMS

The problems of the thin layer begin already in the preparation stage, since the structure, properties, and frequently the very presence of the ferroelectric effect depend decisively on the method of synthesis.

There are many methods for the preparation of thin layers: mechanical grinding, chemical etching, slip casting, various kinds of sedimentation, vacuum condensation, etc. The choice of the method depends on the specific problem. For example, the method of deposition on to a support of a suspension of microcrystallites obtained by grinding the starting material is convenient for the structural analysis of the film by electron diffraction. Grinding, casting, and sedimentation are used for the preparation of thick films. Studies on thin films require methods such as vacuum condensation, etc.

A simple method for reducing the thickness of films is mechanical grinding, but this yields high-quality films with a thickness not less than 50–100 μm. Thinner films (15–20 μm) are prepared by slip casting[15-17]. The slip is prepared from a fine-grained powder synthesised beforehand and having the specified composition. The main fraction of the powder must consist of particles smaller by a factor of 5–10 than the thickness of the cast film. The composition of the binder is chosen on the basis of the conditions governing the optimal formation of the slip, adequate elasticity, and fluidity. The slip is spread on a cleaned support and after drying the film is sintered. The method requires an apparatus for vacuum treating the slip and is used in the mass production of film devices.

One of the sedimentation methods is cataphoresis[18,19] which involves the deposition of the powder from a suspension and subsequent sintering of the layer. The deposition is sometimes carried out in an electric field[20–23] or with the aid of a centrifuge[24]. Films with thicknesses ranging from 5 μm upwards can be prepared by fusion. The initial material is fused on a platinum foil in a specific atmosphere and spreads on the support with formation of a strong single-crystal film[26]. An unusual method involves evaporation from solution; a thin layer of barium titanate consisting of individual crystallites has been prepared in this way[27].

The decrease in thickness by chemical etching involves treatment of a massive specimen (or a single-crystal plate), subjected to preliminary grinding, with a solvent capable of slow dissolution of the material. Hot orthophosphoric acid is used for barium titanate. The method makes it possible to obtain films with a thickness down to 500 Å, but it is then extremely difficult to achieve a uniform thickness. Such layers are used in electron microscopy[28–30]. Single-crystal films with a thickness of several hundreds of ångströms have been prepared by a suspension method[31], but this procedure cannot yield layers with a smoothly varying thickness. The preparation of vitreous layers in a high-temperature flame has been described[32,33].

Methods involving vacuum condensation on a thoroughly cleaned support have found extensive application in the preparation of ferroelectric films. There is a large literature (monographs, reviews, articles; see for example, Refs. 34–36) on this problem. The thickness of the condensate is varied within wide limits, including monatomic layers.

Depending on the method of sputtering of the initial ferroelectric substance, the following procedures can be distinguished:

1. Thermal sputtering by high-temperature heating using a resistance furnace and electron or laser beams[37–40].
2. Cathodic sputtering in which evaporation is achieved by bombarding the substance with inert gas atoms accelerated by a constant field generated by two electrodes (diode sputtering[41]) and by the fields of radiofrequency (RF-sputtering) or high-frequency (HF-sputtering) generators[42–48,68]. When a gas is added to the inert plasma, reactive sputtering takes place[49,50].

We shall now compare the characteristics of thermal and cathodic sputtering. Films prepared by cathodic sputtering require a smaller amount of the starting material, since the target is used repeatedly. Compared with the thermal method of evaporation, cathodic sputtering of compounds having a complex composition ensures a somewhat better stoichiometric composition. Having established the required atmosphere, the second method makes it easier to obtain, for example, oxide films free from an oxygen deficiency. Finally, substances can be subjected to cathodic sputtering over a wide range of temperatures.

On the other hand, the method of thermal sputtering has many undoubted advantages. A simpler equipment is used without the need for a high voltage and exact metering of the gaseous atmosphere, without the difficulties associated with the regulation of the discharge, and without field interference. The rate of condensation is appreciably higher than in cathodic sputtering. Homogeneous films of complex geometry and with a thickness varying in accordance with a specific law are more readily obtained. The thickness of the films is more easily regulated and reproducibility and continuous process control can be more readily achieved. It is significant that thermal evaporation yields purer films compared with cathodic sputtering, in which the rate of adsorption of residual gases may exceed the rate of adsorption of the material condensed. Thus the choice of the method of vacuum condensation depends on the specific material, the specific properties of the films, and technical feasibility.

In the thermal evaporation of ferroelectric materials of complex composition, the so called method of "discrete" evaporation, sometimes referred to as the "instantaneous", "explosive", or "grain-by-grain" method, is most common. It was first used to prepare brass films[51] and was then extended to many materials, including complex oxides with a perovskite structure[52].

The essential feature of the method is that the substance is supplied to the evaporator in small discrete doses. Because of its low heat capacity, each dose vaporises fairly rapidly, creating a vapour with a nearly stoichiometric composition. The condensation of this vapour on the support should give a stoichiometric composition. Under specific condensation conditions, there are additional parameters influencing the composition. For this reason, a modification of the method is used (involving a change in the form of the evaporator, variation of the rate of supply of the material, variation of the composition of the starting material, the introduction of oxygen into the growing film, etc.[39,53,54]).

Compared with other procedures for the preparation of thin films, the vacuum condensation methods have advantages, such as the possibility of smooth control of the thickness (which can reach that of a monatomic layer) and other characteristics of the film by changing the type of support, its temperature, the rate of deposition, etc. The methods of vacuum condensation have been applied on a technological scale and can be used in mass production. A common disadvantage of these methods involves the problem of stoichiometry and structural ordering, which arise from the non-equilibrium conditions in the condensation process.

On the other hand, vacuum condensates have a structure which frequently cannot be generated by other methods (ultrasmall ordered regions with strong disorientation, saturation by defects). This makes it possible to use such films as model systems for the investigation of the influence of the degree of order, the proportion of defects, and other factors on the ferroelectric properties of the substance.

III. THIN BARIUM TITANATE FILMS

1. Atomic and Supra-atomic Structures

Films prepared by methods which do not involve the cleavage of the starting material to the atomic-molecular level (as in vacuum condensation) do not exhibit appreciable changes in atomic structure within the framework of the structural motif. They can be single crystals, can be obtained by chemical etching of crystals, or by the fusion method, or they can have a polycrystalline structure if they are prepared, for example, by sedimentation methods. While it is evident that the perovskite motif is retained in such barium titanate layers, the problem of spontaneous deformation (c/a) in the thin film is not so clear. It is known[55] that low-temperature synthesis of $BaTiO_3$ leads to a cubic cell ($c/a = 1.00$) and not to a tetragonal cell. The grain dimensions then do not exceed 0.1 μm,[39,56] but suppression of spontaneous deformation is not attributed to the small size of the structural elements but to structural defects in the substance: lattice vacancies[55] and layers of the hexagonal phase[39].

On the other hand, the decrease of the normal spontaneous deformation in particles having a diameter less than 1 μm has been explained[57] by a kind of domain configuration of such very small grains. In the same study an anomaly was observed in the spontaneous deformation in a surface layer 100 Å thick, where c/a exceeded the normal value for barium titanate. This anomaly persists up to 600°C. A similar effect has been described in a study[58] where the tetragonal structure of the surface layer did not disappear up to 430°C. This situation was accounted for by the presence of a thin layer of space charge[59]. Another interpretation[60] involves a change in the composition of the atomic layers near the surface, which becomes close to that of TiO_2 in consequence of the opposed shifts of the Ti and O atoms. However, it remains obscure why the increase of c/a in the thin layer is not manifested in small $BaTiO_3$ crystals, where the role of the surface layer should be considerable.

Electron microscope and electron microdiffraction studies on thin (about 500 Å) barium titanate films[28,29,61] failed to reveal anomalies in c/a or significant deviations from the positions of the atoms in the lattice relative to massive material. This can indicate either errors in the earlier experiments[57] owing to the inadequate resolution of the electron diffraction pattern, as suggested by Tanaka and Honjo[28], or an effect operating in a layer several ångströms thick. On the other hand, appreciable structural changes in the surface layer may be caused by the applied electric field owing to the non-linear distribution of potential[62]. The layer of inhomogeneous deformation caused by the increase of the parameter c and the decrease of a expands with increase of field strength. This fact can explain the contradictions between electrophysical and structural studies (the former revealed anomalies in the surface layer and the latter did not) and also between the data of different workers concerning the thickness of the anomalous layer.

In contrast to the group of studies discussed above, investigation of the structure of vacuum condensates revealed the possibility, in principle, of a dependence of their structure on the conditions of synthesis. Depending on the type and temperature of the support, the rate of condensation, and the stoichiometry, different degrees of ordering, and different types of variation of the size, shape, and orientation of the grains are obtained[38,43,52,63-67,69-73]. In condensation on a cold (t_{room}) support, a disordered structure arises in the $BaTiO_3$ film and the diffraction lines on the X-ray and electron diffraction patterns are diffuse. The nature of the structure of such a film remained obscure for a long time; it was not clear whether it is a result of random shifts of the atoms from their normal positions within the limits of each unit cell (intrinsically amorphous state) or whether it is a normal atomic configuration within the limits of several unit cells with distortion of long-range order (a highly dispersed state). A direct study of the structure by the radial distribution method in combination with high-resolution electron transmission microscopy[74,75] established that the film consists of disoriented regions whose size amounts to several tens of ångströms. The perovskite motif persists within each region, but the interatomic distances deviate somewhat (up to 5%) from their values in the crystalline film as the coordination sphere increases (Fig. 1). The structure of amorphous films with an excess of barium is appreciably different[76].

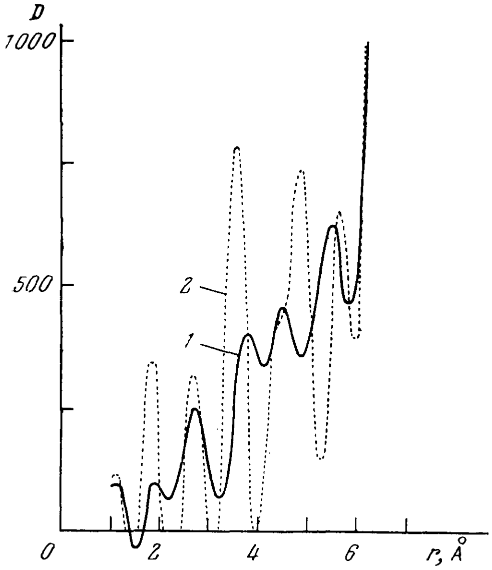

Figure 1. Atomic radial distribution functions D in disordered (curve *1*) and crystalline (curve *2*) barium titanate condensates[74,75].

Structural ordering leading to crystallisation is mainly initiated by the action of heat on the condensate, which the latter can experience during film growth or subsequently. The nature of the crystallisation is different in the two instances and different temperatures are required for the same degree of crystallisation: during subsequent annealing, the temperature must be higher by several hundreds of degrees than the temperature of the support during condensation[38,74,76]. The formation of the structure of the $BaTiO_3$ film on a heated support has been studied by many workers[52,63,65,74,77,78]. At a certain temperature of the support (130–500°C), which depends on its type, the rate of condensation, and the residual atmosphere, crystallites, usually rectangular in shape, begin to develop in the disordered matrix. With increase of temperature, the crystallites grow, filling the matrix, and lose their crystallographic outline in the plane of the film. The orientation of these formations on supports made of ionic crystals is as a rule $\langle 100\rangle \parallel \langle 100\rangle$. $\{111\}$ twins on an LiF support[79] and the $\langle 111\rangle \parallel \langle 111\rangle$ orientation on a platinum foil[18] have also been noted. In crystalline regions, the interatomic distances in the pseudocubic approximation are close to those for the massive crystal[74,76,80]. Thus the condensate obtained on a heated support has a characteristic microstructure: it comprises single crystal regions distributed in a disordered matrix. In many cases the single-crystal "islands" have the same azimuthal orientation, giving rise to an epitaxial effect[52,74,76,77,79] (Fig. 2).

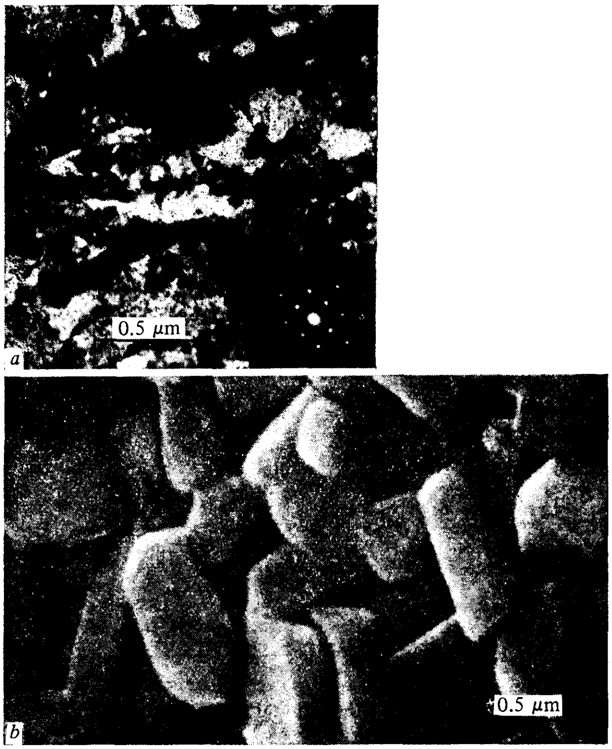

Figure 2. Photomicrographs of a section of barium titanate condensate obtained in different ways: *a*) on a lithium fluoride support heated to 850°C (the diffraction pattern is shown in the lower right-hand corner); *b*) on a cold platinum support with subsequent annealing at 1300°C for 2 h.[74,80]

The causes of the partial retention of disorder in the matrix lie in the considerable proportion of defects in the condensate which are not eliminated by heating. The defects are due primarily to the non-stoichiometry of the film, admixtures of the evaporator material, and other factors[39,74]. Some of the defects serve as centres for the formation of sections with a random orientation.

Heat treatment (starting from $t = 500-1000°C$ [38,64,74,81]) of the condensates obtained on a cold support ensures more homogeneous crystallisation, which is revealed by X-ray diffraction. Annealing at 1200–1400°C tends to order the structure, promoting the transition from the cubic to the tetragonal modification and the growth of grains, the size of which can reach between a few tenths of a micrometre to tens and hundreds of micrometres depending on the thickness of the film[39,74,78,82,83] (Fig. 2). The negative influence of high-temperature annealing consists in the growth of crystals of an impurity, which is present in the matrix in a finely dispersed state after condensation[74,84], and also in the formation of cavities between the crystallites in consequence of intense coalescence processes[64,74,81].

The condensates obtained have a polycrystalline or orientated structure with the direction of texture <100> or <111>.[18,38,39,46,83,85]

The high degree of order does not always guarantee the occurrence of spontaneous deformation in the condensate. In many instances[38,39,86,41,47] the formation of a cubic and not a tetragonal phase at room temperature has been claimed. The transition from the disordered state to a tetragonal structure probably proceeds via the cubic modification. In massive barium titanate, the conversion of the cubic cell into the tetragonal cell occurs at 800° to 1050°C,[39,55,74] while in thin condensed films the transition is delayed, so that $c/a = 1.00$ in some regions of the film even after annealing at 1200–1300°C.[38,41] The quenching of the high-temperature cubic phase in the films can be explained by the appreciable degree of supercooling in the condensation process[84,86,87]. The degree of spontaneous deformation in thin layers is as a rule close to the normal value (~1%),[38,39,41,65,88] although the possibility of the variation of c/a in some cases is not ruled out[83].

The absolute values of the unit cell parameters in the films are usually close to the parameters of the massive material in the pseudocubic approximation. At room temperature, $a = 4.01 \pm 0.02$ Å,[41,88] 4.000–4.030 Å,[39] and 3.99–4.02 ± 0.01 Å.[74] An increase of the parameter by up to 2% after condensation on a support at $t < 900°C$ has been noted[41] (Fig. 3).

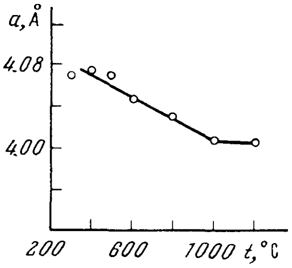

Figure 3. Variation of the unit cell parameter a (in the pseudocubic approximation) of barium titanate films with the temperature of the support t (according to Shintani and Tada's data[41]).

On the whole, one must emphasise that the inadequate resolution of the X-ray diffraction patterns of the condensates preclude a rigorous analysis of the multiplicity of the lines and accurate measurements of the parameters. It is therefore possible that fine structural effects are undetected.

2. Composition

The problem of the composition, which is particularly important for condensed films, did not receive adequate attention for a long time. There is reason to believe, for example, that the stoichiometry of the thin layers obtained in the frequently quoted investigations[89,90] was appreciably distorted. The suppression of the ferroelectric effect in consequence of the imperfection of the composition and structure of the condensates masks size phenomena. The gap in studies on the compositions of thin barium titanate layers was probably due to the lack of a suitable measuring technique.

In recent years, following the development of electronic probe analysis, a wide variety of X-ray microspectroscopic studies on thin condensates have become possible (the study of the local and total composition, of the distribution of elements, of the thickness, etc.). Methods have been developed for the absolute determination of the stoichiometry in terms of the concentrations of the individual elements of the film [91,92] as well as simpler methods in which the composition of the film is compared with a standard using the ratio of the intensities of the spectral lines [66,93]. It is convenient to employ for $BaTiO_3$ the ratio of the Ba $L\alpha$ and Ti $K\alpha$ lines. The standard value is $I_{\text{Ba}\,L\alpha}/I_{\text{Ti}\,K\alpha} = 0.83 \pm 0.05$ for an accelerating potential of 20 kV. [66] The thickness of the layer is determined at the same time from the intensity of the spectral lines of the constituent elements of the film or the support [93,96].

The stoichiometry of the condensates depends on the composition of the molecular vapour, the rate of condensation, the type and temperature of the support, the residual atmosphere, and other parameters. Although the mechanism of evaporation has not been completely elucidated, mass-spectrometric data [82,99] and other considerations [66] indicate a complex composition of the vapour, which contains, together with $BaTiO_3$ "molecules", also BaO, TiO_2, and reduced "fragments", down to metal ions (Tables 1 and 2). Naturally, the complex composition of the vapour phase must have a significant influence on the stoichiometry of the barium titanate condensates. Indeed, there is evidence for the presence of an excess of barium oxide [39,88] in condensed films of the higher oxides $BaO.nTiO_2$ ($n = 2-4$), Ba_2TiO_4, and $BaWO_4$. [38,64,97] The non-stoichiometry of the $BaTiO_3$ condensates prepared by discrete evaporation has been investigated in detail [66,74,98].

Table 1. Composition of the barium titanate vapour under "stationary" conditions* determined mass-spectrometrically (according to the data of Verbitskaya et al. [32]).

Evaporation temp., °C	Material of evaporator	Composition	
		effusion chamber	open surface
2200	Tungsten cell	BaO^+, TiO_2^+, TiO^+, WO_2^+, Ba^+, $BaTiO_3^+$	—
1820	Tungsten cell and strip	BaO^+, TiO_2^+, TiO^+, WO_2^+, Ba^{+2}	BaO^+, TiO_2^+, TiO^+, Ba^+
1980	Iridium strip	—	BaO^+, TiO_2^+, TiO^+, Ba^+

*Under "pulse" (discrete) evaporation conditions, the $BaTiO_3^+$ concentration increases by a factor of 10.

Regardless of the condensation parameters, the films contain different amounts of excess barium ($I_{\text{Ba}\,L\alpha}/I_{\text{Ti}\,K\alpha} > 0.8$), which has an unfavourable influence on the microstructure, being segregated in the form of droplike inclusions. When material with an excess of titanium introduced beforehand is evaporated [53], oxides with a high titanium content are distributed in the matrix without hindering the growth of the perovskite $BaTiO_3$ phase. This can be explained by the crystallisation of $BaTiO_3$ over a wide range of existence, according to the $BaO-TiO_2$ phase diagram [100].

Table 2. Mass-spectrometric composition of the vapour of barium titanate evaporated by the discrete method (according to Nurriddinov's data [99] and the studies quoted in his paper).

Ion	Ba^+	BaO^+	TiO^+	TiO_2^+	$BaTiO_2^+$	$BaTiO_3^+$	WO_3^+	WO_2^+
Relative intensity	0.8	1.0	0.3	0.1	0.06	0.1	0.1	0.08

The favourable role of the excess titanium had been noted earlier [38,101], albeit without any explanation of its causes, for films obtained by evaporation from individual BaO and TiO_2 sources as well as by Feldman's method [37,102]. Films with an excess of titanium ($I_{\text{Ba}\,L\alpha}/I_{\text{Ti}\,K\alpha} = 0.3$ to 0.8) have a structure fairly close to ideality and exhibit ferroelectric properties. Impurities can be identified after high-temperature annealing. As a result of local fluctuations, BaO, Ba_2TiO_4, $BaTi_2O_5$, $BaTi_3O_7$, $BaTi_4O_9$, and sometimes an impurity from the evaporator material have been detected in $BaTiO_3$ condensates. General analysis of the problem of the stoichiometry of $BaTiO_3$ condensates [98] has shown that it is apparently extremely difficult to obtain a rigorously stoichiometric composition.

In addition to the deviation from the stoichiometric proportions of barium and titanium, a deficiency of oxygen is frequently observed in the films, oxygen being lost partly on evaporation of the initial powder and partly on condensation, particularly on a hot support. As a result of the loss of oxygen, some of the Ti^{4+} species are reduced with formation of "defect electrons" and an increase of electronic conductivity. The oxygen deficiency can be eliminated by annealing the film in air or in oxygen at temperatures up to 500°C.

3. Structural Defects

The films, particularly those obtained by condensation, contain an appreciable amount of structural defects. An attempt to give a systematic account of the lattice defects in barium titanate vacuum condensates has been made [74].

Point, linear, and three-dimensional defects are formed during preparation. The first type includes (a) atoms displaced from normal positions and "frozen" following condensation on a cold support, (b) impurity atoms, including "excess" structural atoms present due to non-stoichiometry (local X-ray spectroscopic analysis has revealed between 0.1 and 1 wt.% of the evaporator material), and (c) oxygen vacancies formed under reducing condensation conditions. Other types of defects include the boundaries between the crystallites and the disordered matrix and between the grains as well as microscopic cracks arising in consequence of the relaxation of microstresses as well as cavities produced by coalescence processes.

Table 3. Certain ferroelectric parameters of barium titanate films*.

Method of preparation	Structure	d, μm	ε	tan δ	f, Hz	P_s, μC cm-2	E_c	E'	References
Melt	Single crystal	20	4000—6000		50	—	—	—	26
»	»	2—100	100—1000	—	—	2, 2, 5	—	—	121
Etching	»	1—100	600—5000 (at 125°C)		2—200·10^3	—	—	—	107
»	»	3.5—97	—	—	—	5—25	10	—	108
Sedimentation followed by annealing	»	6.7—38.5	500—2000	—	10^3	1—4.5	—	—	18
Electrophoresis	Polycrystalline	0.5—180	⩽820	0,01	—	—	—	—	109
Vacuum condensation	»	2.7	50—1200	—	—	—	7,5	100	78
»	»	10	⩾100	—	—	—	2	—	110
»	»	1.5	300	0.1—0.2	—	0.5—1	—	—	81, 97
»	»	5—7	1100	0.02—0.03	—	—	—	—	82
»	»	0.1—1	20—1330	0.04—0.26	10^3	—	—	10^2—10^3	38
»	Textured	<1	1580	0.04	—	10	100	—	45
»	Polycrystalline, textured	1—12	400—1200	0.02—0.05	10^3	1—14	—	5·10^2—10^3	83
»	Polycrystalline,	0.08—2	28—270	—	1.5·10^6	5.4—6.4	20	100	111, 88, 112
»	Textured	⩾1	—	—		several units	60—80	—	85
»	Polycrystalline, textured	0.5—10	200—600	—	—	9—16	20—40	—	39
»	ditto	0.8—1.2	20—130	0.05—0.15	10^3	—	—	—	46
»	Polycrystalline	2	1700	0.018	10^3	0.2	—	—	41
»	»	0.2—1.25	110—215	0.02—0.05	10^3	—	—	>100	50, 113
»	»	—	150—1500	0.02—0.5	10^3—10^6	—	—	—	114
»	»	0.05—1	400—1500	—	—	—	—	—	115
»	»	3—10	400—1200	0.02—0.05	2·10^3	8—12	—	—	116
»	Polycrystalline, textured	0.5—10	10—2000	—	—	—	—	—	44
»	»	0.2—1	50—350	0.02—0.08	10^3	—	—	>100	47
»	»	0.5	300	0.5	10^3	—	—	—	66
»	»	0.3	1200	0.4	10^3	9	—	—	74
»	»	0.01—0.5	30—1000	0.4—0.5	10^3—10^4	2—10	—	—	117
»	»	0.1—0.35	176—1020	0.05—0.12	10^3	—	—	5·10^2	40
»	»	1—4	100—3000	⩽0.1	—	—	—	—	223, 224
»	Textured	2.5	450 (t=120° C)	⩽0.15	10^3	7—8	20—40	—	225

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*d = thickness, ϵ = dielectric constant at room temperature, tan δ = dielectric losses at room temperature, f = frequency, P_s = spontaneous polarisation at room temperature, E_c = coercive field, and E' = dielectric strength.

Structural defects impair and in many cases suppress the ferroelectric properties of the thin layer, the mechanisms of the influence of the defects being various. Presumably the inhibition of the transition from the cubic to the tetragonal structure of the condensate[86] is caused particularly by defects of the point type. There is apparently an analogy between the cubic phase of the films and the radiation-induced cubic modification of massive barium titanate, arising after irradiation with neutrons above the threshold dose of about 10^{18} neutrons cm^{-1}.[103-106] This phase does not exhibit a low-temperature transition to the polarised state and probably lacks ferroelectric properties[103]. The cause of the transition to the cubic phase and of the stabilisation of the latter is believed to be the point defects formed after mixing the atoms. Only prolonged annealing at 1100—1200°C restores the tetragonal structure of the material[105]. Under these conditions, some of the defects are not annealed, which is indicated by an increase in the lattice parameters. Presumably similar processes occur also in condensates.

4. Ferroelectric Properties

The degrees of spontaneous polarisation, dielectric constants and losses, coercive fields, and other ferroelectric parameters of the barium titanate films, based on the data of different investigators, are presented in Table 3. The scatter of the results can be explained by the very great sensitivity of the properties of the thin layer to its previous history (the technology of the preparation and attachment of the electrodes, the electrode material, and the conditions of the measurements). It is necessary to distinguish clearly technological factors, which determine the proportion of structural defects in the films, from size effects.

The influence of structural defects. The "impairment" of the ferroelectric properties of the thin layer compared with the initial barium titanate (the decrease in the degree of spontaneous polarisation, the increase of the coercive field and the dielectric losses, the blurring of the phase transition, etc.) are due primarily to the "dilution" of the ferroelectric phase by regions which are incapable or only partly capable of transpolarisation—the regions of the lattice with zero spontaneous deformation, non-stoichiometric phases, and extraneous inclusions[74,86,98,108].

The dielectric constants of the films depend significantly on relaxation polarisation processes of different types and on the surface states[117, 118]. Monomolecular gaseous and organic films on the surface of a ferroelectric material form surface layers with unstable characteristics. The removal of these layers before the deposition of electrodes ensures an adequate reproducibility of the properties[107]. The role of the relaxation mechanisms is manifested in the low frequency dispersion of ε and tan δ characteristic of condensates[38,40,44,78,89,118]. The decrease of the dielectric constant and dielectric losses with increase of frequency may be considerable (Fig. 4).

The nature of the ferroelectric phase transition in a thin layer, particularly a condensed layer, is not quite so marked as in massive $BaTiO_3$. The degree of blurring of the transition is determined by heterophase fluctuations in composition (for condensates) or other fluctuations. However, with the exception of cases where a solid solution based on $BaTiO_3$ is formed in the condensate, the Curie temperature T_C (120°C) is maintained to within 5 to 10 K.[97,102,107,116,117] This fact indicates the existence in the condensates, in addition to the defective regions, of highly ordered regions with spontaneous nearly normal deformation ($c/a = 1.01$). Thus, in contrast to radiation-induced damage, the structural defects are not distributed homogeneously in the condensates. This factor can in fact explain the different types of behaviour of T_C in the films and in irradiated ferroelectric materials. The defects in the condensates influence the degree of blurring of the phase transition, without altering T_C significantly; on the other hand, radiation damages each cell, causing a decrease of c/a and an appreciable shift of T_C towards lower temperatures.

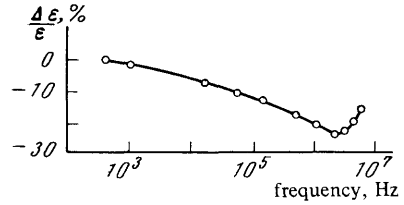

Figure 4. Variation of the dielectric constant of the $BaTiO_3$ condensate with frequency[44].

Size effects in films. The results of studies on the ferroelectric parameters of thin films, which may be treated as the manifestation of dimensional effects, although in many instances technological factors cannot apparently be fully ignored, are considered below.

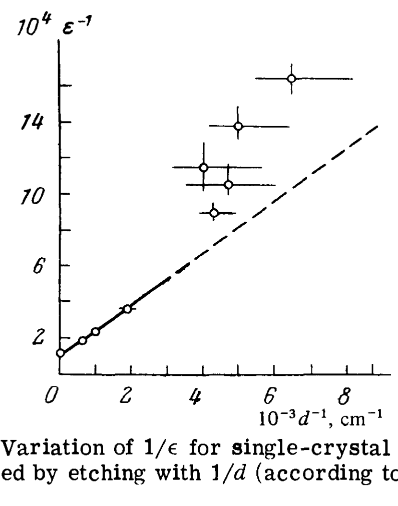

Figure 5. Variation of $1/\varepsilon$ for single-crystal $BaTiO_3$ films obtained by etching with $1/d$ (according to Makarov's data[107]).

The dependence of the dielectric constant on the thickness of single crystal films obtained by the attenuation method has been studied in a series of investigations[25,26,107,119-122]. At an early stage it was concluded that ϵ increases as the thickness of the layer is reduced[26], but subsequent studies by the same and other investigators showed that the variation of ϵ with d is linear down to $d \simeq 3.5$ μm, a deviation from the relation being observed below this limit[107,119,123,124] (Fig. 5). The decrease of ϵ is caused by the decrease of the effective Curie–Weiss temperature[107]. The Curie–Weiss constant is independent of the thickness of the crystal in the range $1 \geqslant d \geqslant 4000$ μm.

The coercive field in the tetragonal phase increases with decrease of d,[25,122] but in low-temperature modifications the increase is not quite so great. An increase of P_s in a thin layer (up to 6 μm) relative to a thicker film has been observed[121]. However, later the same authors concluded[25,119] that the dependence of P_s on thickness is weak for $d \geqslant 1$ μm. According to these data, the tetragonal structure and transpolarisation persist down to 1 μm in accessible fields. The absolute degree of spontaneous polarisation is appreciably reduced compared with massive $BaTiO_3$. The decrease of P_s in films prepared by deposition followed by sintering has also been noted by other investigators[18], although in this case the defects probably played an appreciable role. In layers with $d \leqslant 10$ μm, obtained by etching, a monotonic decrease of the degree of spontaneous polarisation with thickness was demonstrated[108].

The smoothing of the $\epsilon(t)$ relation with decrease of thickness has been noted[121]. For $d = 1$ μm, the maximum in the $\epsilon(t)$ relation at 120°C disappears, but reappears in a stronger field, albeit in a diffuse form. The retention of $T_C \simeq 120$°C for $d \geqslant 1$ μm is significant[120].

The smoothing of the maximum in the $\epsilon(t)$ relation near 120°C with decrease of d has been noted[25]. A similar effect has also been observed in thinner layers prepared by condensation[117] (Fig. 6). For a $BaTiO_3$ vacuum condensate with a thickness of 100 ± 20 Å, the $\epsilon(t)$ maximum in the region of 120°C is completely smoothed out, while both low-temperature maxima are retained.

It must be emphasised that the increased proportion of defects in condensed layers does not rule out the possibility of using them for the investigation of size effects, for example, the dependence of dielectric parameters on thickness. A set of films with different thicknesses, obtained under similar condensation conditions (identical proportions of defects), made it possible to determine the $P_s(d)$ relation in the range $100 \leqslant d \leqslant 1400$ Å (Fig. 7).[117] At room temperature, P_s decreases with thickness from about 10 μc cm^{-2} ($d \geqslant 1400$ Å) to approximately zero for $d \simeq 100$ Å. The thinnest ferroelectric layers (100–200 Å) have apparently been obtained in a study by the present author and Sevost'yanov[117].

5. The Theory of Size Effects in $BaTiO_3$

The decrease in the size of an object below a certain limit leads to a change in its properties (the size effect). The critical size is different for different properties.

The theory of the size effect in ferroelectric materials is based on thermodynamic and microscopic concepts, which permit a qualitative (at best semiquantitative) description of the critical phenomenon. For ferroelectric materials, the concept of the critical size is related to parameters such as spontaneous induction D_s (polarisation P_s) and deformation, the Curie temperature T_C, the dielectric constant ϵ, the domain structure, etc.

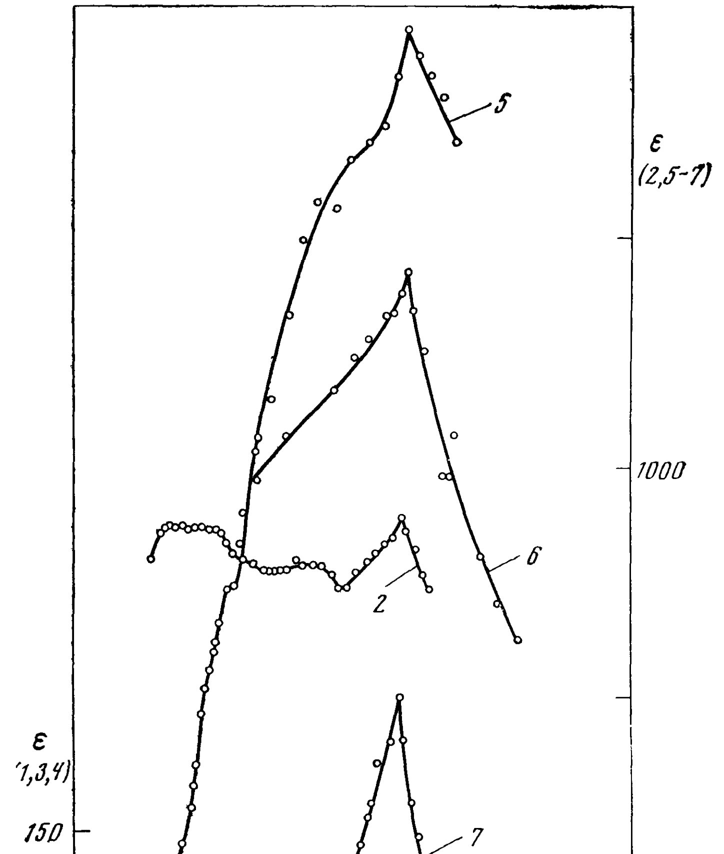

Figure 6. Temperature variation of ε for barium titanate condensates with different thicknesses (Å): 1) 100; 2) 230; 3) 430; 4) 450; 5) 680; 6) 800; 7) 5000 (according to Tomashpol'skii and Sevost'yanov's data[117]).

In depolarisation field models[125–132], the presence of an incompletely shielded depolarisation field E_{det}, directed in opposition to P_s, is postulated in a thin C-domain crystal. Ivanchik[125] took into account the mechanism of shielding by free carriers alone. At equilibrium, characterised by a minimum in the free energy F, the latter is expanded as a series (the usual procedure in a formal thermodynamic treatment) in terms of the spontaneous induction D_s (polarisation) with retention of higher terms and differentiation with respect to the expansion parameter.

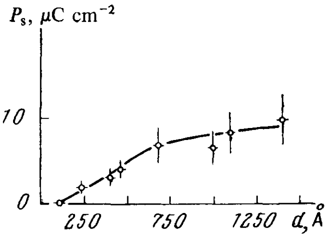

Figure 7. Experimental variation of P_s with d for barium titanate condensates (according to Tomashpol'skii and Sevost'yanov's data[117]).

The assumption of partial conductivity of the crystal makes it possible to express the electric field E in terms of the charge density, which is in its turn a function of D_s. Thus a closed equation, the solution of which determines the dependence of the ferroelectric parameters on the thickness of the crystals d, is obtained for D_s (or P_s). Apart from the semiconductor shielding mechanism, others, for example, mechanisms associated with structural defects, have also been proposed[126].

Ivanchik's ideas[125] were subsequently extended to a ferroelectric–electrode system with a distributed space charge[127–131], more detailed account being taken of the influence of the electrical contact conditions: the material of the contacts and methods for achieving them.

The depolarisation field model yields a relation between P_s, T_C, and d. An estimate of the critical thickness (corresponding to the complete disappearance of the effect) leads to 200–500 Å for barium titanate[125,132]. This approach explains qualitatively the experimentally observed decrease with thickness of P_s and the pyrocoefficient γ and the blurring of the phase transition. However, the model is not free from disadvantages, which hinder a quantitative interpretation of experimental data. The assumption of semiconducting properties implies the presence in the ferroelectric of a definite number of free carriers, which contribute to the shielding E_{dep} and promote its "dissipation". It has been noted[133] that a prolonged action of E_{dep} in conducting crystals is unlikely and its numerical value is "the subject of a major controversy"[130]. Furthermore, the theoretical conclusion that T_C is appreciably displaced towards lower temperatures with decrease of d has not been confirmed experimentally for $BaTiO_3$ down to thicknesses of about 200 Å.[117,119] No account is taken in the model of surface states[134], which can have an appreciable influence on the redistribution of polarisation charges owing to their partial or complete compensation on the surface[135]. Finally, the model is valid only for the C-domain state, whereas in reality one encounters, apart from the C-domain configurations[136,137], also A-domain thin layers[29,111,119], for which the influence of E_{dep} is not significant[138].

According to the dynamic model[119,120], in which the lattice vibrations of a ferroelectric plate with a limited thickness d in the z direction are considered under the conditions of a transverse frequency ω_t, the dielectric constant ϵ_z should decrease with decrease of d, while ϵ_x and ϵ_y should remain invariant. T_C does not change significantly.

In a monoaxial ferroelectric ($P_s \| z$), a phase transition would be impossible for a certain thickness. In the case of $BaTiO_3$ the presence of three equally valid directions of P_s should lead to the conversion of the thin layer into the A-domain form and only a weak variation of P_s with thickness. Thus the dynamic model does not predict significant changes of P_s for thin crystals of the $BaTiO_3$ type or a shift of T_C with decrease of film thickness. According to the model, the Curie–Weiss temperature and the dielectric constant decrease for low values of d, while the $\varepsilon(t)$ relation is smoothed out owing to the ϵ_z component. The limitations of the model involve, in particular, the fact that its conclusions are valid only for the thickness range $1 \leqslant d \leqslant 300$ μm.[120]

In the electrostatic model of the thin layer of a ferroelectric material[117,139], one considers the dependence on thickness d of fields due to dipoles and charges and the Lorentz (E_{Lor}) and depolarisation (E_{dep}) fields in C- and A-domain films of the barium titanate type. The behaviour of the internal electric fields E_i and of spontaneous polarisation P_s with decrease of d is determined by the relative contributions of the opposed E_{Lor} and E_{dep} fields. The Lorentz field begins to decrease with decrease of the thickness below the critical value, which has been estimated as 300–500 Å, depending on the chosen size of the Lorentz cavity. When $d <$ 300–500 Å, the model predicts an appreciable decrease of E_i and P_s. If $E_{dep} = -4\pi P$ (P is the polarisation), i.e. is not shielded, then $P_s \rightarrow 0$ when a = 80–100 Å for a C-domain film. When E_{dep} is weakened or absent (an A-domain crystal), a low value of P_s persists for $d < 100$ Å. The model does not rule out the occurrence of spontaneous polarisation in layers with a thickness below 1000 Å and yields a $P_s(d)$ relation which can be reconciled with experimental data[117] for a suitable choice of parameters. The inadequate rigour of the criteria governing the choice of the critical thickness makes the model semiquantitative.

A fairly simple model, which explains the anomalies in the ferroelectric properties of thin crystals, is that of the surface layer[57,112,123], based on experimental evidence for its existence. Regardless of their nature, surface layers are considered anomalous from the standpoint of ferroelectric behaviour. A thin crystal is treated as a layer condenser, the internal component of which consists of the "normal" ferroelectric and the outer regions consist of the "anomalous" material (with a low value of ϵ, a high coercive field, etc.)[123,124]. The overall value of ϵ, which decreases with decrease of film thickness for a constant depth of the surface layer, is calculated in terms of this scheme.

The model explains the decrease of ϵ, the smoothing of the $\epsilon(t)$ relation in the region of the phase transition, the increase of the coercive field, and other anomalies in the film. However, one must point out certain experimental data which are difficult to account for within the framework of this model. Kanzig and coworkers[57] suggested that the surface layer model is based on the structural distortions within the cell. On the other hand, electron microscope[28], electron microdiffraction[61,140,141], and X-ray[142] studies failed to reveal such distortions in the crystals (with thicknesses down to 500 Å) and in the surface layer of $BaTiO_3$ with a thickness of hundreds of ångströms. The presence of a strong electric field in the surface layer[62,143,144] should lead to an increase of the concentration of C-domains near the surface. However, as stated above, experimental data indicate a tendency by thin films (where the surface layers should have an appreciable negative volume) towards conversion into the A-domain form[29,111,119]. In the surface layer model, its non-ferroelectric nature (low values of ϵ, high coercive fields, the absence of transpolarisation, etc.) is usually emphasised. Direct observation of the domain structure of $BaTiO_3$ with the aid of a scanning electron microscope[145] indicates a ferroelectric behaviour of the regions near the surface. Finally, the results of different studies concerning the depth of the surface layer h and its dielectric constant ϵ are characteristically contradictory (h = 0.01 to 25 μm, ϵ = 5–1080).[59,112,123,124,135,146-152]

Evidently the depth of the surface layer (if it exists) is not a single-valued film parameter, depending on many factors (mechanical treatment, heat treatment, the applied field, irradiation with light, etc.)[3,58,153]. It has been noted correctly[120] that the surface layer model is very flexible, because it operates with a number of adjustable parameters. However, the uncertainty of the parameters introduced precludes the use of the model for a rigorous quantitative comparison with experiment.

The ferroelectric characteristics of thin layers (in particular vacuum condensates) can be calculated using a model the ferroelectric properties of which are determined by the degree of "dilution" of the ferroelectric phase by non-polarised regions, without specifying the nature of the latter: this may be a quenched high-temperature phase, defective regions where there is no transpolarisation, and extraneous impurities. P_s for such a mixture can be calculated within the framework of the electrostatic model from the effective atomic shifts[74,86] and the dielectric constant can be found from the formulae of Grossman and Isard[154].

Thus theoretical analysis explains the dimensional effect in thin ferroelectric layers: the decrease of P_s, ϵ, and γ, the blurring and shift of the phase transition (T_C), and the change in the lattice vibration spectrum.

The theory predicts a critical film thickness, below which $P_s = 0$. The specific form of the relations between the ferroelectric characteristics and the critical size on the one hand and d on the other is a function of a number of parameters (conductivity, electrode material, the surface state, the domain structure, etc.). In the depolarisation field model, the critical thickness is 200–500 Å and in the electrostatic model 80–100 Å (for a C-domain film in the absence of shielding from the depolarisation field).

6. $BaTiO_3$ Films as Models in Studies of the Ferroelectric State

Determination of the critical size of ferroelectric "nuclei". In the model of ferroelectric nuclei[155], it is assumed that small regions of the tetragonal modification arise in the deep paraphase, grow with decrease of temperature to T_C, reaching the critical size, and below T_C are converted into a system of 180-degree domains. Bearing in mind that the cessation of the growth of the "nuclei" before the attainment of the critical size (when the latter exists) owing to restriction by the natural grain boundaries should lead to the suppression of the "normal" ferroelectric behaviour (dimensional effect), an attempt has been made[156] at an experimental determination of the critical size of the region of the tetragonal phase in barium titanate. Condensed films where there is a possibility of an extensive variation of the grain size, from tens of ängströms to hundreds of micrometres are unique models for such research.

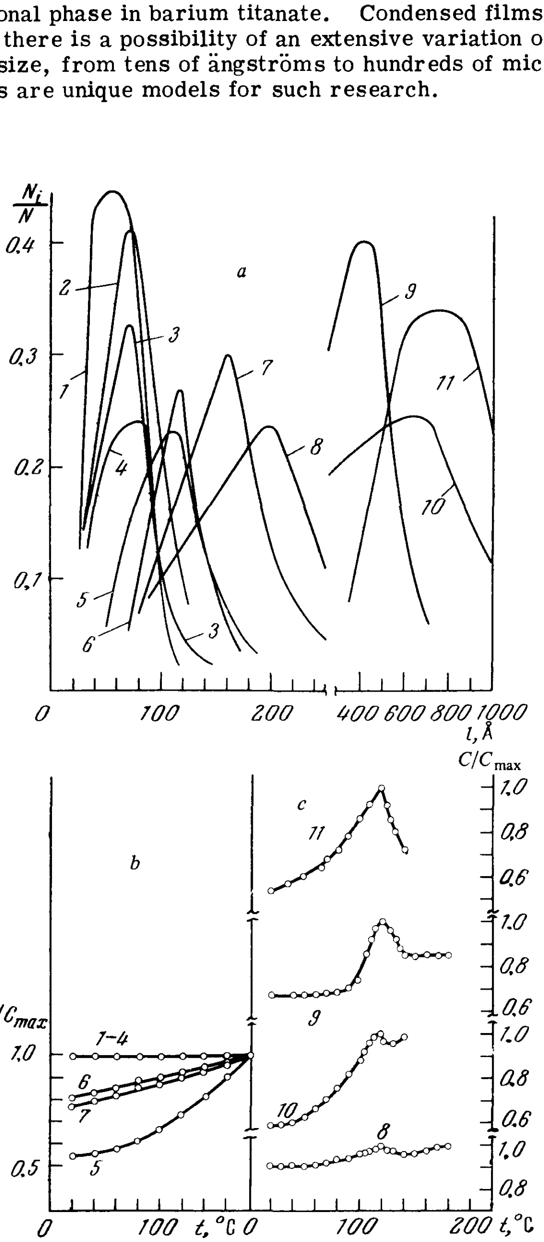

Figure 8. Distribution of grains (N_i/N) with respect to size (a) and temperature variation of the relative capacitance C/C_{max} (b and c) of condensed barium titanate layers (according to Tomashpol'skii and Sevost'yanov's data[156]); the numerals opposite the curves in the lower part of the figure correspond to the numerals in its upper part.

Fig. 8 presents the results of dielectric measurements on films with different average grain sizes, which show that there exists a limiting grain size $l \simeq 180-250$ Å, below which there are no ferroelectric anomalies and which may be compared with the critical "nucleus". The experimental critical size is satisfactorily correlated with the size of the fluctuation regions in the vicinity of T_C, observed by Kanzig[157] and calculated theoretically in a number of investigations[158–161].

Determination of the group velocity of phonons in the ferroelectric mode. The decrease of the dielectric constant has been explained by a change in the bulk-phase vibrations in thin ferroelectric layers[119]. In this approach, the experimental study of the size effect in films makes it possible to determine certain parameters of the dynamic model for those regions of the phonon spectrum where ultrahigh-frequency and neutron spectroscopic methods are ineffective. A high velocity of phonons has been obtained from the dielectric constant of single-crystal barium titanate films: $\sqrt{B} \simeq 10^7$ cm s^{-1} (B is a constant related to long-range forces in the dynamic theory)[107].

IV. FILMS OF SOLID SOLUTIONS BASED ON BARIUM TITANATE

The characteristics of films of the solid solutions Ba(Ti, Sn)O_3 and (Ba, Sr)TiO_3 with a thickness in the range 10–500 μm, obtained by the slip casting method, have been investigated in a number of studies[124,162,174], while others, prepared by the grinding method (30–35 μm thick), by etching (with a thickness from 40 μm upwards), and by cataphoresis (approximately 80 μm thick), have been investigated by Morozov[163], Burfoot and Sensordenker[164], and Yamanaka et al.[165] respectively. For $d \geqslant 30$ μm, the coefficient of non-linearity, ϵ, and P_S remain high[162,174]. However, for $d < 30$ μm, the coefficient of non-linearity and other parameters decrease. As the thickness is reduced below 500 μm, the controlling potential falls, which makes it possible to employ non-linear film elements based on (Ba, Sr)TiO_3 in semiconductor circuits[124]. The ultrahigh frequency dispersion in the ferroelectric phase and the maintenance of the validity of the Curie–Weiss law in the paraphase have been observed[163]. Certain optical characteristics of thick films with 25% Sr have been published[164].

In the preparation of solid solution vacuum condensates, additional problems associated with stoichiometry arise. The contradictory nature of the data obtained for condensed films is associated primarily with the inadequate control of their composition and structure. Thus, an increase of the dielectric constant with decrease of thickness from 1.6 to 0.1 μm, has been reported[89], the absolute value of ϵ amounting to several thousands. $\epsilon < 50$ has been obtained for similar films in another study[90]. The validity of the results of a particular investigator is difficult to establish, since the composition of the condensate was not followed in either study. (Ba, Sr)TiO_3 films 2–3 μm thick have been obtained[78] by the method of discrete evaporation and $\epsilon(t)$ maxima, displaced towards lower temperatures compared with pure BaTiO_3, have been observed. Low-frequency dispersion has been found in the range 10^2-10^6 Hz. $P_S < 1$ μC cm^{-2} has been obtained at room temperature for a $(Ba_{0.95}Sr_{0.05})TiO_3$ film 2.4 μm thick.

(Ba, Sr)TiO_3 vacuum condensates with a thickness less than 1 μm have been obtained and investigated in a series of studies[118,166–168]. The structures and compositions were determined by X-ray diffraction and by local X-ray spectroscopic analysis. In order to correct for the excess barium and strontium, the initial material had a composition with a barium deficiency[53]. The structure of the films was of the perovskite type with parameters close to that of the starting material, provided that the multiplicity of the X-ray lines was disregarded. The ferroelectric behaviour of the solid solution condensates was confirmed by the dielectric hysteresis [$\epsilon(t)$ peaks], which disappeared at temperatures above those of the phase transitions. As for massive specimens, the $\epsilon(t)$ maxima shifted towards lower temperatures with increase of the strontium content. The limiting thickness of the solid solution film in which transpolarisation was still observed amounted to about 700 Å.

The decisive influence of structural ordering and stoichiometric factors on ferroelectric properties has been demonstrated and it has been shown that the structural defects in the films initiate relaxation processes. Spontaneous polarisation coexists under the conditions with relaxation polarisation, the contribution of which may be fairly high. A characteristic feature of the films is a high value of $\tan\delta$ (amounting to several tenths at low frequencies), low frequency dispersion, and the blurring of phase transitions.

(Ba, Ca)TiO_3, Ba(Ti, Sn)O_3, Ba(Ti, Zr)O_3, and (Ba, La)TiO_3 condensates have been investigated[42,167,169]. After heat treatment, admixtures of TiO_2 and other phases are detected in the films together with the perovskite modification. Following the addition of 14% La or Ca, T_C falls to room temperature. The difference between the values of ϵ for the film and the massive material does not exceed 5% and the dielectric losses amount to 0.01 to 0.03. For (Ba, La)TiO_3 condensates obtained by cathodic sputtering[169], $\epsilon \simeq 200$ (at a frequency of 1.5 kHz) and $\tan\delta \simeq 0.02$ dielectric strength $\simeq 10^5$ V cm^{-1}.

V. OTHER COMPLEX OXIDE FILMS

1. Strontium Titanate ($SrTiO_3$)

The preparation of strontium titanate vacuum condensates among other perovskites materials was reported for the first time by Muller et al.[52] Thin layers obtained by cathodic sputtering were investigated in greater detail by Pennebaker[49], who found that, when this method is used, the properties of the films are influenced mainly by the size of the crystallites and the oxygen pressure. Although many properties of the condensate proved to be similar to those of the starting material, nevertheless ϵ amounted to 65% of the value for massive $SrTiO_3$ and the losses were appreciably higher. The variation of ϵ and $\tan\delta$ with thickness and dielectric strength of 500 kV cm^{-1} have been observed[170] for films obtained by the same method.

The structures and properties of strontium titanate films 0.05–1 μm thick, prepared by the method of discrete evaporation, have been investigated in detail[171-173]. The principal parameter determining the stoichiometry with respect to strontium and titantium is the rate of condensation, which leads to an excess concentration of strontium when it exceeds the optimum value ($\leqslant 1$ Å s^{-1}). Condensation on a heated support is responsible for the appreciable losses of oxygen from the film compared with condensates deposited on a cold support. The oxygen deficiency can be partly or completely compensated by subsequent annealing in air or in oxygen.

In the disordered state, the film consists of a collection of arbitrarily oriented regions whose size amounts to several tens of ängströms. Within each region, the perovskite motif is maintained but the interatomic distances are somewhat different from those in the massive crystal. High-temperature treatment results in ordering processes leading to crystallisation. In the crystalline state, the unit cell parameters are close to the initial values (for the massive specimen). At low temperature, the behaviour of the $\epsilon(t)$ relation is different for the disordered and crystalline films. For the former, ϵ falls slowly with decrease of temperature, and for the latter it increases, although more slowly than the value for the initial crystal. At −100°C and a frequency of 1 kHz, $\tan\delta = 0.01-0.001$ in disordered films and the dielectric strength is $\sim 10^6$ V cm^{-1}.

2. Lead Titanate ($PbTiO_3$)

Condensates 0.1–0.3 μm thick have been prepared by the cathodic sputtering method[175]. In order to achieve a stoichiometric composition, the lead content in the target did not exceed 5%. The dielectric constants ϵ of these films amounted to several tens. Films with structures closer to ideality, prepared by the same method, had dielectric constants which depended on the molar ratio Pb : Ti and amounted to about 500 in the optimum case (1 : 1).

3. Lead Zirconate ($PbZrO_3$)

Thick $PbZrO_3$ layers have been prepared by deposition in a constant electric field[22,176]. Their dielectric constants are several times smaller than the values for polycrystalline specimens and the dielectric losses are higher in consequence of the porosity of the layers. A shift of T_C towards higher temperatures has been observed.

4. $(Pb_{0.92}Bi_{0.07}La_{0.01})(Fe_{0.405}Nb_{0.325}Zr_{0.27})O_3$

Films 2–16 μm thick with a perovskite structure and having the above complex composition have been obtained by deposition followed by sintering[177]. For these layers, $\epsilon \simeq 1000$ and $T_C = 150$°C. The degree of spontaneous polarisation amounts to 10–20 μC cm^{-2} and the coercive field is $\geqslant 15$ kV cm^{-1} with a satisfactorily rectangular hysteresis loop. One of the films of this series withstood 2×10^{11} switchings lasting 300 ns at a potential of 20 V.

Studies on films of the same composition, prepared by radiofrequency sputtering, have been reported recently[178]. For films 4.5 μm thick, it has been found that $\epsilon \simeq 1600$, $P_S = 3-15$ μC cm^{-2}, the coercive field is 5–10 kV cm^{-1}, $T_C \simeq 80$°C, and the resistance is $\sim 10^{14}$ Ω cm. The condensates withstood 10^{11} switchings lasting 200–600 ns without appreciable changes in P_S and the coercive field.

5. Calcium Titanate ($CaTiO_3$)

Vacuum condensates 0.1–0.3 μm thick with $\epsilon = 20-60$ have been obtained[179]. Their high dielectric strength (up to 10^7 V cm^{-1}) is striking. The structures and properties of the films, prepared by discrete evaporation, have been studied[180]. The unit cell parameter in the pseudocubic approximation is $a = 3.90 \pm 0.05$ Å, which somewhat exceeds the values for massive $CaTiO_3$ ($a = c = 3.819$ Å and $b = 3.815$ Å); the dielectric constant is 500–700 (for the initial ceramic, $\epsilon = 200$), but the dielectric losses in the films are higher ($\tan\delta = 0.5$ against 0.2 in the massive specimen). The electret properties of ceramic calcium titanate films have been studied[181]. An electric field has not been detected in the films in the presence of an appreciable space charge.

6. Tungsten Trioxide (WO_3)

The microstructure and certain physical properties of WO_3 condensates have been described[182]. The films were deposited *in vacuo* (10^{-5} mmHg) on glass supports. The observed characteristics are complex functions of technological parameters.

7. Lithium Niobate ($LiNbO_3$) and Lithium Tantalate ($LiTaO_3$)

Foster[183] reported studies on lithium niobate films 2–4 μm thick obtained by cathodic sputtering. The condensates proved to be weakly textured, had $\epsilon = 65$ at a frequency of 1 kHz and a piezoelectric coefficient of about 0.08, which is about 50% of the value for a single crystal along the z axis. The preparation of $LiNbO_3$ and $LiTaO_3$ films by high-frequency sputtering has been described[47,184]. The authors observed a deficiency of lithium in the film and enriched the target in lithium for the purpose of compensation. The ferroelectric properties of these condensates are weak: $\epsilon = 80-100$ and $\tan\delta \simeq 0.1$.[47] The elements of the epitaxial growth of $LiNbO_3$ condensates with the (001) orientation, prepared by discrete evaporation on a single crystal layer of silver, have been determined[185]. Attempts have been made to grow single-crystal $LiNbO_3$ films for optical purposes[186].

8. Ferroelectric Niobates

Thin layers having the $KNaNb_2O_6$, $Ba_2NaNb_5O_{15}$, $K_3Li_2Nb_5O_{15}$, and $PbNb_2O_6$ compositions have been obtained by cathodic sputtering on SiO_2 supports coated with gold[187]. The stoichiometry was maintained to within 10–15%. A weak piezoelectric effect was observed in some of the films.

9. Bismuth Titanate ($Bi_4Ti_3O_{12}$)

Epitaxial layers of bismuth titanate have been obtained[188–191]. The condensation temperature was varied from 400° to 700°C and the target consisted of a ceramic with an excess of bismuth to compensate for its losses. The thickness of the films on MgO and platinum supports was 0.2–4.5 μm. The dielectric characteristics, including the degree of spontaneous polarisation, agree well with the values for the massive crystals. Domain boundaries were observed in films 12–32 μm thick[189].

10. Lead Germanate

The discovery of the ferroelectric effect in lead germanate was reported recently[192,193]. The new ferroelectric belongs to the trigonal system, the threefold axis is polar, and $T_C = 170-180$°C. According to the authors[192,193], the formula of the ferroelectric crystal is $5PbO.3GeO_2$, but one cannot rule out a somewhat different composition, namely $3PbO.2GeO_2$.[194,195] Polycrystalline lead germanate films with a thickness <1 μm and having a structure and composition close to those of the initial single crystal have been prepared by discrete evaporation and investigated[196]. An anomaly in the $\epsilon(t)$ relation, corresponding to the phase transition in the massive crystal (T_C), and a dielectric hysteresis loop were observed. The degree of spontaneous polarisation is about 70% of its value for the single crystal.

11. Strontium Tellurate ($SrTeO_3$)

A characteristic feature of this new ferroelectric is that its ferroelectric properties are observed in the temperature range 312–485°C.[197] Films about 0.1 μm thick were obtained by the vacuum evaporation of the comminuted ceramic $SrTeO_3$, for which the temperature range of the polarised state was found to be 325–470°C.[198] Polycrystalline layers can be made even when the support is at room temperature. Heat treatment of the films in air leads to a distinct maximum on the $\epsilon-t$ curve at 470°C, corresponding to T_C for the ceramic. A lower limit of the ferroelectric region was not observed.

12. Antimony Orthoniobate ($SbNbO_4$)

Antimony orthoniobate, a new ferroelectric material, has $T_C = 403$°C and $P_S = 15$ μC cm^{-2} at room temperature, according to Lobachev et al.[199] $SbNbO_4$ vacuum condensates, obtained by discrete evaporation, have a polycrystalline structure[200]. The $\epsilon(t)$ relation has a maximum in the region of 380°C. For the films with the composition closest to stoichiometry, dielectric hysteresis was observed at room temperature; $P_S = 7.4$ μC cm^{-2} and $\tan\delta = 0.1-0.5$.

It has been reported recently[201] that $SbNbO_4$ is an antiferroelectric above 403°C and that the transition to the paraelectric region (T_C) occurs at 600°C.

VI. FERROMAGNETIC VACUUM CONDENSATES

The combination of ferroelectric and ferromagnetic dipoles in a structure of the perovskite type has been achieved in a ceramic consisting of solid solutions of ferroelectric–ferromagnetic systems[202,203], one of the components of which is the $Sr_{0.3}La_{0.7}MnO_3$ solid solution with the magnetic Curie point $T_C^M = 90-120$°C.[204,205]

Condensates of the $BaTiO_3-Sr_{0.3}La_{0.7}MnO_3$ system have been investigated[206]. Films approximately 1000 Å thick with the composition close to $(Ba_{0.9}Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ were prepared by discrete evaporation, varying the composition of the starting material and subjecting the film to heat treatment during and after condensation. The composition and structure were investigated by local X-ray spectroscopic and X-ray diffraction analyses.

Fig. 9 illustrates the temperature variation of the relative dielectric constants ϵ/ϵ_{max} and of the half-widths ΔH of electron spin resonance lines for films of the initial components $BaTiO_3$ and $Sr_{0.3}La_{0.7}MnO_3$ as well as the condensate of the above composition. The $\epsilon/\epsilon_{max}(t)$ maximum, corresponding to the ferroelectric Curie point T_C, is displaced from 120°C for the pure $BaTiO_3$ film towards lower temperatures following the addition of $Sr_{0.3}La_{0.7}MnO_3$. The $\Delta H(t)$ minimum, corresponding to T_C^M (90°C)[207] for the $Sr_{0.3}La_{0.7}MnO_3$ condensate, also moves to the region of lower temperatures. Thus $T_C^M = -120$°C and $T_C^E \leqslant -130$°C were obtained for the $(Ba_{0.9}.Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ films. Compared with a ceramic of similar composition and also with films of the initial components, the transitions in the ferromagnetic film are diffuse and occur at lower temperatures, probably owing to fluctuations in composition.

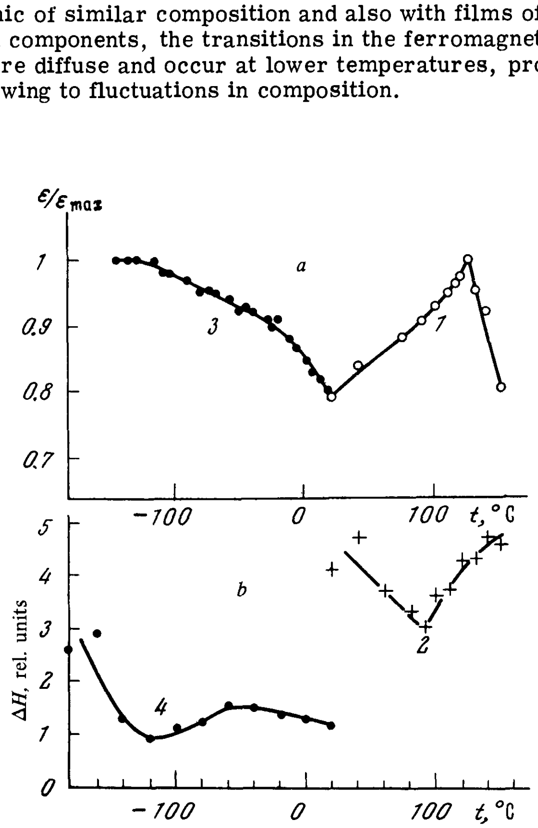

Figure 9. Temperature variation of the relative dielectric constant ϵ/ϵ_{max} (*a*) and electron spin resonance line half-width ΔH for the manganese ion (*b*) in films of the initial components $BaTiO_3$ (curve *1*) and $Sr_{0.3}La_{0.7}MnO_3$ (curve *2*) and the condensate $(Ba_{0.9}Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ (curves *3* and *4*)[206].

VII. CERTAIN APPLICATIONS OF THIN FERROELECTRIC LAYERS

The need for thin ferroelectric layers in a wide variety of electrical and optical instruments as condensers, pyroelectric detectors, piezoelectric transducers, memory elements, and indicator elements is fairly considerable[13,14]. It has been concluded[208] that one of the important applications of ferroelectric films may be their use as condensers for microwave amplifiers in multimodular systems. The requirement for a high value of ϵ and a low value of $\tan\delta$ at high frequencies is important here. $BaTiO_3$ and $PbTiO_3$ films are therefore less suitable for such purposes than, for example, $Bi_4Ti_3O_{12}$ condensates. The latter ensure a high capacitance (0.02–0.2 μF) and low dielectric losses up to frequencies of about 10^9 Hz. Condensed $SrTiO_3$ films with $\epsilon = 200$ also exhibit low dielectric losses up to 10^9 Hz.[49] Thus bismuth and strontium titanate films can be used as microwave condensers by virtue of their frequency characteristics and the comparatively low temperature at which they are prepared (<600°C), which is compatible with other technological operations.

It has been established[209] that thin layers of ferroelectric oxides with added lanthanum, having high and positive temperature coefficients of resistivity, can be used as sensitive detectors of infrared radiation. After annealing at 1400°C, a $Ba_{0.600}Sr_{0.397}La_{0.003}TiO_3$ film 10 μm thick had a resistivity of $\sim 10^6\ \Omega$ cm and a temperature coefficient of resistivity of ~6%. High annealing temperatures are an obstacle in the technology of the preparation of such elements for infrared video devices, but in the search for new thermistor compositions, technological progress should lead to the solution of this problem[210].

The pyroelectric materials usually employed as sensitive thermodetectors and in thermal vision systems consist of single crystals or ceramics, but the optimum thickness of such elements in thermal vision is 10–15 μm, i.e. the element should be a film. A decrease of thickness gives a higher sensitivity, a better resolution, and low inertia[211]. One of the problems arising in connection with the use of pyroelectric materials in such devices involves difficulties in the preparation of electrically and optically homogeneous elements of large size.

Piezoelectric elements made of massive ferroelectric materials are widely used as electromechanical transducers in acoustic arrest lines, but their comparatively large size limits their use to low frequencies. It has been shown[212] that elements ~1 μm thick are necessary in devices where the transducer operates as a generator or detector of ultrasonic waves at frequencies of ~10^9 Hz.

Thus ferroelectric films with high electromechanical coupling coefficients, such as $LiNbO_3$, lead zirconate-titanate, and alkali and alkaline earth metal niobates with the structure of tungsten bronzes can be used in such applications. Positive results have been obtained[183] on oriented $LiNbO_3$ films prepared by cathodic sputtering, in which the (012) plane of the hexagonal structure is inclined at an angle of 40° to the support. Piezoelectric measurements on thin films yielded a piezoelectric coefficient of 0.08, which amounts to about 50% of its value for the single crystal. The reasons for the difference are probably associated with the non-stoichiometry and inadequate structural ordering of the condensates.

By analogy with ferromagnetic materials, the ferroelectric hysteresis loop has a potential application in memory devices. It has been shown[177,213-216] that memories with capacities up to 10^9 bits can be achieved with the aid of thin photoconducting and ferroelectric layers. The thickness of the $(Pb_{0.92}Bi_{0.07}La_{0.01})(Fe_{0.405}Nb_{0.325}Zr_{0.27})O_3$ layers used, prepared by ceramic casting and sputtering[217], reached several micrometres, the ferroelectric films exhibiting a rectangular hysteresis loop and satisfactory thermal scattering. The memory device was charged by means of a light spot focussed on the screen of a cathode ray tube.

The use of thin ferroelectric layers in image-producing devices requires structures in which the contrast of the image, caused by the variation of double refraction under the influence of an electron beam modulated by the video signal, is not too sensitive to the thickness of the element. Here the most suitable material is bismuth titanate in which the optimum contrast can be achieved for a particular growth orientation. Since natural $Bi_4Ti_3O_{12}$ crystals do not grow in the required [crystal] habit, a solution was found to the problem when layers of the *A–C*-domain crystal with a large area (1 cm²) were grown on MgO and $MgAl_2O_4$ single crystals[188,189,191]. An example of the use of a non-linear ferroelectric capacitance and of hysteresis properties in image-producing devices is provided by a system comprising a liquid-crystal matrix and a thin transparent plate of a CTS ceramic with added lanthanum[218].

Among other applications, mention should be made of the use of ferroelectric films as indicator devices[219] and light modulators ($LiNbO_3$ and $LiTaO_3$)[220,221] and also for dielectric thermostabilisers and other purposes[222].

In conclusion one should note that, as a result of the efforts made in recent years to study the mechanisms of growth and ordering processes and to extend and improve preparative methods, there has been a clear progress in the technology of the preparation of highly ordered ferroelectric films, including epitaxial layers. However, many problems, on the solution of which depends the attainment of optimum properties (stoichiometry and homogeneity of composition, epitaxial growth, physical material of the electrodes, and methods of their deposition), are still far from a complete solution. There is a need for more far-reaching studies of the surface phenomena in ferroelectric materials, the role of which is particularly significant in a thin layer.

There has been an appreciable increase in the number of new ferroelectric films. Whereas the vast majority of studies were previously concerned with barium titanate, in recent years more than 20 new compounds and solid solutions have been obtained as films, including bismuth titanate, lead germanate, and antimony orthoniobate. Here efforts should be directed towards the search for compositions which do not require high temperatures of synthesis and which possess the necessary properties.

In practical applications there has been a transition from the predictive stage to the incorporation of thin-layer ferroelectric elements in solid state devices. The optimum technology has been developing vigorously recently. Further progress in research on thin ferroelectric layers will reveal new fields for their application.

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During the preparation of the manuscript for the press, numerous studies were published on the synthesis and applications of thin lithium niobate layers. $LiNbO_3$ films have been prepared by decomposing the vapours of organometallic compounds on lithium tantalate supports[226], by dipping the support in an $LiNbO_3$ melt[227], by diffusion into the region of the surface layer of the crystal[228-234], and by ion exchange[235]. Similar systems have been proposed as optical and acoustic waveguides and electro-optical modulators[230,231,236-246]. The applications of films as waveguides have been reviewed[247,248].

Memory devices based on films with an epitaxial structure (bismuth titanate), synthesised by high-frequency sputtering, have been made[249,250]. The possibility of devising capacitive film heat sensors has been demonstrated[251]. New data for size effects in ferroelectrics and their treatment in thin layers have been published[252,253] as well as data obtained in studies on $SrTiO_3$ and (Ba, Sr)TiO_3 vacuum condensates[254-256]. Methods have been developed for the measurements of the dielectric parameters of ferroelectric films in the ultrahigh frequency range[257].

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Intramolecular Coordination in Organic Derivatives of Non-transition Elements

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The problem of intramolecular coordination in organic derivatives of non-transition elements is surveyed and critically considered. Only those inner complexes (in an unreacting molecule or in the transition state)where the chain with the donor atom is linked to the element only via carbon atoms are considered. The data are treated systematically on the basis of the type of ligand. It is shown that intramolecular coordination is the driving force in various molecular rearrangements and many elimination reactions involving organic derivatives of the elements.
The bibliography includes 331 references.

CONTENTS

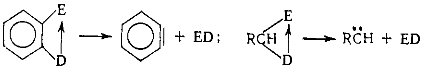
I. INTRODUCTION

Twenty years have elapsed since the synthesis of the first stable organic derivatives of the elements with intramolecular coordinate bonding in which the chain containing the donor atom is linked to the non-transition acceptor element only via carbon atoms. They have been called inner complex organic derivatives of the elements[1]. The comparatively sluggish development of this field can be explained both by the lack of clear-cut criteria concerning the understanding of the very concept of intramolecular coordination (IAMC) and by the defects of the current physical and physicochemical methods for the determination of the structure of matter and the consequent serious difficulties in the detection and demonstration of IAMC.

IAMC should be understood as a donor-acceptor interaction with charge transfer within the limits of a single molecule taking place through space, by-passing the conjugation chain, and involving the formation of a new single D-E bond in the limiting case (D is the electron-donating atom and E the non-transition acceptor element). Naturally one excludes from consideration a similar interaction between two adjacent atoms of the type of $d_\pi - p_\pi$ conjugation, for example in aminoboranes and silylamines, which might be regarded as a special case of IAMC resulting in only an increase of bond order.

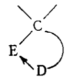
The strength of IAMC in a non-reacting molecule is unknown, since no inner complex for which the conformational equilibrium constant has been determined has so far been described. Nevertheless most investigators suggest that intramolecular coordination interaction is energetically close to hydrogen bonding. The limits of its manifestation are fairly wide: from complete charge transfer, as, for example, in γ-aminopropyl compounds of boron, to closed structures in which IAMC occurs only in the transition state.

The available data on the properties of organic derivatives of the elements with IAMC were reviewed for the first time in 1970[2]. Their importance for theory and practice in the chemistry of organic derivatives of the elements was already noted at the time. In subsequent years these compounds were successfully used in the synthesis of reactive and unstable species such as carbenes and arynes, the synthesis of which by other methods is in many instances impossible. Reactions of this kind, proceeding via IAMC, have been described by Nefedov et al.[3]:



In the present review we shall therefore not consider β-elimination in aromatic systems with formation of arynes and α-elimination in aliphatic systems with formation of carbenes.

The aim of the present review is to survey data on the physical and chemical properties of organic derivatives of non-transition elements with IAMC. We shall consider only compounds in which the chain containing the donor atom is linked to the acceptor element via carbon atoms, i.e. true organic derivatives of the elements with IAMC:



The data reviewed are arranged systematically on the basis of the type of ligand, which we believe to be most convenient for the detection of differences in the acceptor properties of elements, and are dealt with in order of decreasing electron-donating capacity of the ligand subgroups in the sequence $\geqslant$N >-O- >-Hal π-systems. This series is purely conventional and changes markedly as a function of the element and the reaction conditions for ligand atoms, belonging to different subgroups, linked to the same hydrocarbon groups. At the same time practice has shown that the ease of formation and the stabilities of many organic derivatives of the elements increase in this sequence. Each type of ligand is discussed in order of increasing size of the rings formed in IAMC, the elements being considered in order of their increasing valence within a Period and downwards within the limits of a single subgroup. The chemical consequences of IAMC are surveyed after coordination in non-reacting molecules has been examined.

Particular attention is devoted in this review to X-ray diffraction studies of compounds with IAMC, since the geometrical criterion—the distance between the donor and acceptor atoms—is one of the most clear-cut pieces of evidence for the presence or absence of coordination.

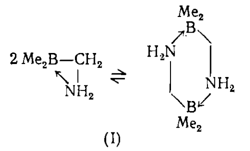
However, this criterion cannot be always justified experimentally owing to the lack of the exact values of the van der Waals radii of the elements in their organic compounds[4]. Furthermore, the radius depends on the hybridisation of the element and can therefore change. Naturally experimental accuracy is frequently the decisive factor and for this reason all studies where it is not indicated have been excluded from this review.

II. INNER COMPLEXES WITH NITROGEN-SUBGROUP LIGANDS

The synthesis of nitrogen-containing organic derivatives of the elements frequently presents considerable difficulties because of the electron-donating capacity of amine and nitrogen and its tendency to form intermolecular complexes. Their number and variety are therefore greatly inferior to similar derivatives of the oxygen and fluorine subgroups.

The presence of IAMC has a significant influence on the physical and spectroscopic properties of organic derivatives of the elements. It is very important to have at ones disposal consistent data obtained by different methods, since only then can one decide sufficiently unambiguously whether or not IAMC is present. This is also associated with the necessity to separate interfering factors such as intermolecular coordination (IRMC), crystal and field effects, solvation, inductive and resonance effects, etc.

Measurements of the molecular weight in the gas phase (13.8% of the dimer at 0°C and pure monomer at temperature exceeding 40°C up to 75°C) and the temperature variation of the ^{11}B NMR spectrum in the liquid phase (decrease of the degree of dimerisation from 84.3% at −25°C to 24.3% at 35°C with a heat of dimerisation of about 9 kcal $mole^{-1}$) have shown that aminomethylboron (I) is involved in a dimer–monomer equilibrium, the amount of monomer increasing with temperature[5]:

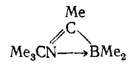


(I)

The study of the dissociation of complexes (I) with trimethylboron and ammonia has shown unambiguously that complex (I) is a weaker acid and a weaker Lewis base than the corresponding monofunctional derivatives. According to ^{11}B and ^{1}H NMR spectroscopic data, the electron density at the boron atom in complex (I) is enhanced compared with trialkylboron and the δ_{CH_2} signal is strongly displaced towards a lower field (by 0.24 p.p.m.; 0.20 p.p.m. in cyclopropane). The combined data quoted above provide serious grounds for the assumption that B ← N intramolecular coordination obtains in the monomeric state of compound (I).

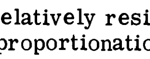
It is noteworthy that[6] dimethylaminomethylboron exists only in the dimeric form up to 170°C. The authors explain this difference from compound (I) by the greater electron-donating capacity of nitrogen in $RNMe_2$ compared with RNH_2, which is in turn manifested by a decrease of the acid properties of dimethylaminoboranes.

The three-membered inner complex obtained in a quantitative yield at room temperature when the product of the addition of trimethylboron to t-butyl isocyanide $Me_3C\overset{+}{N}{\equiv}C\overset{-}{B}Me_3$ isomerises proved to be resistant to the action of oxygen and moisture[7]. The ^{1}H NMR spectrum of the complex was found to contain three signals of the CH_3 group with the line intensity ratios 1:2:3, while the infrared spectrum contains a band with $\nu(N{=}C) = 1548\ cm^{-1}$, but there is no band with $\nu(\overset{+}{N}{\equiv}C) = 2247\ cm^{-1}$. Furthermore, it has been established (by mass spectrometry) that the gas phase contains only the monomeric form of the complex. All these findings confirm the proposed structure[7]:

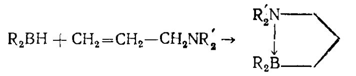


The steric factor is the decisive cause of the formation of the three-membered ring, since the reaction between less hindered isonitriles and boranes leads to the formation of dimeric products—2,5-dibora-2,5-dihydropyrazines[8].

The coordination capacity of the element E in the R_2ECH_2X system (X = Si, Ge, or Sn and X = N, O, S, or a halogen) is extremely low and only one complex, formed by trifluoromethyltrimethyltin with hexamethylphosphoramide[9], has been isolated and weak adduct formed by chloromethyltrimethyltin with dimethylformamide in solution has been described[10]. The latter complex was detected by Mössbauer spectroscopy, although in the organotin compound itself there is no Sn ← Cl intramolecular coordination, as can be seen from the nuclear quadrupole resonance (NQR) spectra[11], Mössbauer spectra[12], and dipole moments[13]. Furthermore, the basicity sequence of the amino-derivatives (Ge > Sn > Si) is consistent with the adopted electronegativity scale of the elements E [14] and there is therefore no coordination even in these compounds. For this reason, the claim[15,16] concerning the occurrence of IAMC in the above system (or the "α-effect") is invalid. According to infrared and ultraviolet spectra, IAMC is also absent from 2-substituted pyridines (E = Si, Ge, or Sn)[17]:

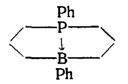


γ-Aminopropyl derivatives of Group III elements cyclise extremely readily to five-membered rings via E ← N intramolecular coordination; in most cases they are obtained by the addition of hydrides to allylamines[18-24]:



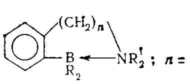
These complexes are relatively resistant to cold water[18], solutions of alkalis[24], disproportionation[22], peroxides[21], mercaptans[23], and heat[22]. Furthermore, they are stable in air and do not react with ammonia and phosphine[21]. In the gas phase, they exist as monomers[21]. The high dipole moments (4.0–4.2 D)[23], high refractions[21], infrared spectroscopic data [$\nu(B \leftarrow N) = 1266\ cm^{-1}$][19], ^{11}B and ^{1}H NMR data[19-21,24], and mass spectra[19,20,24] also indicate the occurrence of IAMC. When the hydrogen atom attached to nitrogen is replaced by alkyl groups or when an alkoxy-group is attached to a boron atom, the strength of the B ← N bond decreases appreciably and in the compound $(EtO)_2BCH_2CH_2CH_2NEt_2$ (μ = 1.44 D) the bond probably does not exist at all[23].

The phosphorus analogue probably also exists in a cyclic form[25]:



This is shown by its stability in air and on heating and by ^{11}B and ^{1}H NMR data.

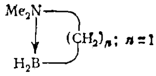
Compounds of the type



; $n = 1, 2$; $R' =$ Alk, Ar; $R = H, NMe_2$, O—

have also been described[26-28]. They too are relatively resistant to hydrolysis and, when $R = H$, do not react with olefins, which is characteristic of complexes with an intermolecular N → B bond[28].

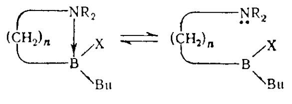
It has been suggested[29] that all compounds of the type



$n = 1$-10

in general involve intramolecular coordination, since their dipole moments are approximately 4 D and the fragments $(M - 1)^+$, where M is the molecular weight, give rise to high intensities in the mass-spectra, this being characteristic of compounds having such a structure; the expected infrared and ^1H NMR spectroscopic properties have also been obtained.

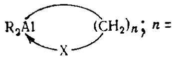
A detailed study of compounds of this class by the ^{11}B and ^1H NMR methods showed that, both in the pure state and in solutions, they consist of an equilibrium mixture of cyclic and linear forms[30-32]:



; $n = 3, 4$; $R =$ Alk; $X =$ Alk, OAlk, SAlk .

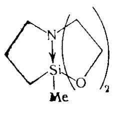
The breakdown and occurrence of intramolecular coordination take place at a rate exceeding $10^3\ s^{-1}$, which enabled the authors[30] to call these compounds a "pulsating" system. The equilibrium position depends on n, R, and X as well as temperature. With increase of temperature, the equilibrium is displaced towards the linear form (as shown by the temperature variation of the ^{11}B NMR spectra and the dipole moments). The equilibrium constants and heats of reaction were calculated from these results.

Similar aluminium compounds are also inner complexes[1,33-35], which are monomeric in hydrocarbons, distil *in vacuo* without decomposition, do not form adducts with ether (for X = OR), and do not form quaternary compounds with methyl iodide (for $X = NR_2$)[1]:

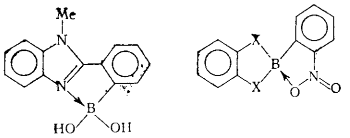


; $n = 3, 4$; $X = NR_2$, OR, SR, Hal .

X-Ray diffraction analysis of methyl(2,2′,3-nitrilodiethoxypropyl)silane confirms the occurrence of IAMC in γ-aminopropyl compounds of non-transition elements even for a relatively poor acceptor such as the silicon atom (reliability index $R = 4.6\%$).[36] The molecule of this compound consists of a distorted trigonal bypyramid with the nitrogen atom and the methyl group at the vertices. The Si–N bond length (2.336 Å) is much smaller than the sum of the van der Waals radii (3.5 Å), but greatly exceeds the length of the covalent bond (1.74–1.78 Å). Steric factors decrease the CNSi angle from the tetrahedral value to 102°, which makes the N → Si linkage relatively long.

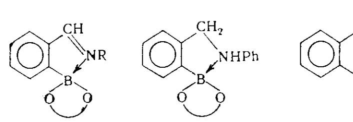


Inner-complex coordination has been put forward to account for the anomalous ultraviolet spectra of the compounds[37,38]



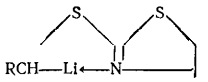
; X = NH, O,

the infrared[39-41] and ^1H NMR spectra[40,41] of the compounds

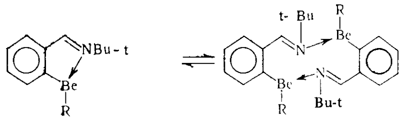


; E=Al, Ga ,

and for the formation of the anomalous products of the reactions of lithiothiazoline[42]:

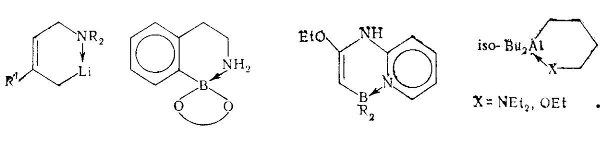


Such coordination is apparently the cause of the *ortho*-metallation of azomethines by dialkylberyllium[43]; in this case, when R = t-Bu, the degree of association of the reaction product in benzene is 1.55–1.65, which suggests the equilibrium



It is also responsible for the *ortho*-metallation of azobenzenes by mercury acetate[44]. These compounds are widely used in the chemistry of transition metals[45].

The formation of six-membered rings as a result of N → E intramolecular coordination takes place with much greater difficulty because of the appreciable angular ring strain. Such ring structures have been proposed for compounds of lithium[46] (on the basis of the stereoselectivity of the reaction products), boron [$\nu(N \rightarrow B) = 1240\ cm^{-1}$,[47] on the basis of infrared and ^{11}B NMR spectroscopic data[48,49]], and aluminium[34]; they are monomeric in benzene solution and thermally stable:

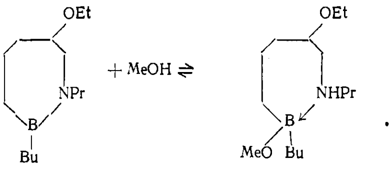


X = NEt₂, OEt .

The instability of the coordinate bond in six- and even seven-membered rings is illustrated by the fact that stable products of the hydroboration of but-3-enyl derivatives containing functional substituents are readily oxidised to alcohols[50]:

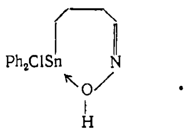
$$CH_2{=}CHCH_2CH_2X \xrightarrow{BH_3} {>}B(CH_2)_4X \xrightarrow{[O]} \text{alcohol};$$
$$X{=}NR_2, OR, SR, OAc, Cl.$$

The rapid dissociation and formation of the N → B intramolecular coordinate bond in substituted 1,2-azaborepanes are reversible and depend both on the concentration of methanol in hexane solutions of the compound and on temperature, as shown[51] by the signal shifts in the ^{11}B NMR spectrum:



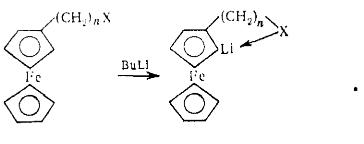
Similar aluminium compounds, iso-$Bu_2Al(CH_2)_5X$ ($X = NEt_2$ or OEt), contain associated species with intermolecular bonds together with seven-membered IAMC structures[34].

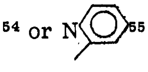
A seven-membered ring is probably formed in δ-stannyloximes, whose infrared spectra, both in the solid state and in solution, contain a $\nu(OH) = 3475\ cm^{-1}$ band, and none due to the hydroxy-groups involved in hydrogen bonding are present. Furthermore, when treated with PCl_5, they undergo a Beckmann rearrangement with exchange of the hydroxy- and stannylpropyl groups, which should therefore be located in the *syn*-positions relative to one another:



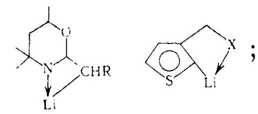
When chlorine attached to tin is replaced by a phenyl group, the compounds behave as the usual ketoximes and do not exhibit the above anomalies[52].

The *ortho*-metallation reactions of ferrocenes and benzenes, with substituents containing atoms having unshared electron pairs (X), and also of heterocycles with the aid of alkyl derivatives of lithium, sodium, and magnesium are of great practical importance from the synthetic standpoint. The high selectivity and high yields of the reaction products can probably be accounted for by the formation of a strong M ← X intermolecular coordinate bond in the initial stages with subsequent metallation in the *ortho*-position and stabilisation of the resulting complexes by an M ← X intramolecular coordinate bond. In most cases lithium alkyls are used as the metallating agents.



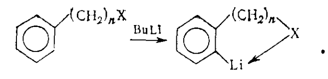
Direct metallation has been investigated in detail for the following amino-derivatives of ferrocene: $n = 1$, $X = NMe_2$,[53] $\langle N(CH_2)_m\rangle$ (m = 4 or 5),[54] or [55]; $n = 2$, $X = NMe_2$.[56] The reactions proceed much more readily than for unsubstituted ferrocene[53]. The evidence for coordination is provided indirectly by the condensation products. These reactions are described in greater detail elsewhere[57,58].

Dihydro-1,3-oxazines[59] and thiophens[60] are just as readily metallated[60]:



; X = NMe_2, OMe .

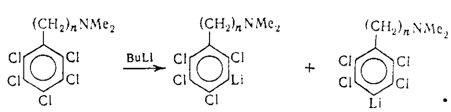
Aminobenzenes are metallated in the *ortho*-position much more slowly and under much more severe conditions than the ferrocene analogues in consequence of the reduced acidity of the protons:



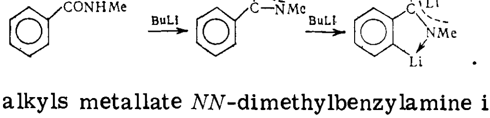
Substituted benzenes have been investigated: $n = 0$, $X = NMe_2$ [61,62]; $n = 1$, $X = NMe_2$ [63]; $X = AsR_2$ [64]; $n = 2$, $X = NMe_2$.[65,66]

The presence of the N → Li intramolecular coordinate bond in such compounds is confirmed by the infrared spectroscopic study[67] of the ^6Li- and ^7Li-labelled benzene complexes ($n = 1$, $X = NMe_2$) in addition to the isolation of *ortho*-substituted reaction products. The $\nu(C-Li) = 355\ cm^{-1}$ and $\nu(N \rightarrow Li) = 494\ cm^{-1}$ bands in the spectrum of the compound with ^7Li were displaced to 370 and 500 cm^{-1} respectively following the introduction of ^6Li. This isotopic shift is characteristic of the N → Li intermolecular coordinate bond and the Li–C bond in ordinary lithium alkyls. Cryoscopic determination of the molecular weight in DMSO showed that at minimal concentrations the degree of association of these complexes is less than 1 but at high concentrations it exceeds 4. An N → Li intermolecular bond is probably formed in the compounds together with the intramolecular coordinate bond. The coordination is confirmed also by the ready removal of DMSO, a powerful solvating solvent, at room temperature *in vacuo*, while ordinary lithium alkyls form stable complexes under these conditions even with ether.

The sharp decrease of the Lewis basicity of the amino-group in *NN*-dimethylamino(alkyl)perchlorobenzenes as a result of the strong electronegativity of the perchlorophenyl group and the impossibility of the formation of an intermolecular coordinate bond with butyl-lithium (particularly in the presence of solvating solvents) lead to their metallation only in the *meta*- and *para*-positions and not the *ortho*-position with respect to substituent[68,69]:

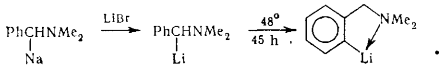


Secondary amines[70], amides[71], and sulphonamides[72] are metallated initially at the nitrogen and only then in the *ortho*-position (in the presence of an excess butyl-lithium), for example:



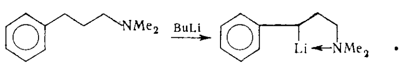
Sodium alkyls metallate *NN*-dimethylbenzylamine in the *ortho*-position with subsequent spontaneous isomerisation to the derivative with the metal in the α-position with respect to the amino-group[73]:

When sodium in the last compound is replaced by lithium, the *ortho*-metallated product can be reformed after prolonged heat treatment, although at room temperature the α-lithio-compound is stable:

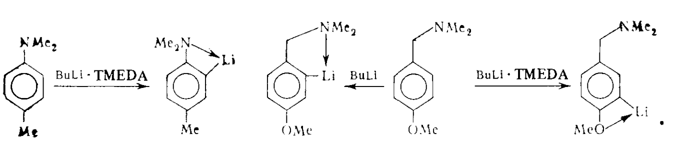


The reasons for these isomerisations are obscure.

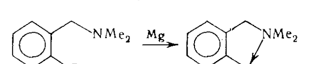
The metallation of *NN*-dimethyl-3-phenylpropylamine proceeds in the chain with formation of a five-membered ring[74]:



One should note that *ortho*-metallation by butyl-lithium proceeds comparatively slowly (11–21 h), but is sharply accelerated (1–2 h) when its complex with tetramethylethylenediamine (TMEDA) is used[75]. On the other hand, the lithium atom in the complex BuLi.TMEDA lacks electron-accepting properties and cannot therefore be involved in an intermolecular coordinate bond with the nitrogen atom of the amino-derivatives of benzene, ferrocene, and heterocycles, which is the main cause of the metallation of the 2-position, and not of the more acidic methylprotons in *NN*-dimethyl-*p*-toluidine [75], and of the *ortho*-position relative to the methoxy-group in *p*-methoxy-*NN*-dimethylbenzylamine. [76] In these compounds the *ortho*- and *para*-directing effects of the dimethylamino- and methoxy-groups exceed respectively those of the methyl and dimethylaminomethyl groups:

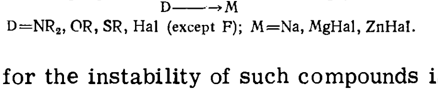


Grignard reagents are also formed very readily (in quantitative yields) from 2-bromobenzyl-*NN*-dimethylamine, while the 3- and 4-bromo-derivatives do not react under analogous conditions[77]:



The chemical manifestations of intramolecular coordination are extremely varied and frequently involve "anomalous" elimination reactions and rearrangements, which do not occur with related compounds where coordination is known to be absent. Furthermore, the metal–carbon σ-bond is polarised under the influence of coordination and therefore becomes more reactive. Such processes are particularly frequent in aliphatic systems.

When alkyl halides containing a heteroatom in the β-position are acted upon by reactive metals, extremely unstable organometallic compounds are formed and decompose at the instant of formation as a result of easy β-elimination[78,79]:

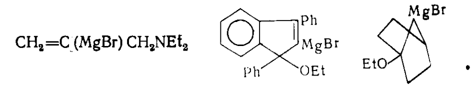


D=NR$_2$, OR, SR, Hal (except F); M=Na, MgHal, ZnHal.

The reason for the instability of such compounds is probably a D → M intramolecular coordinate bond, although this has not been specially investigated.

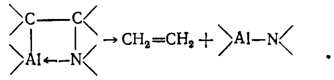
Numerous studies have shown that β-elimination in Grignard reagents cannot be prevented either by very low temperatures or by the protection of functional groups[79].

There are only a few instances of the successful formation of Grignard reagents of this type where either the activation energy for the formation of allenes is unduly high[80,81] or the elimination reaction is forbidden by Bredt's rule[82]:

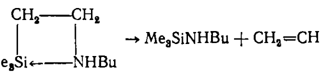


Halogenoamines $R_2N(CH_2)_nHal$ form organomagnesium compounds in THF with $n \geq 3$.[79,83]

The β-aminoethyl derivatives of aluminium, which begin to decompose with formation of ethylene already during their formation when vinylamines add to aluminium hydrides (at 20–60°C), are also unstable[84]:

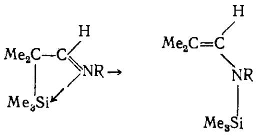


The similar silicon compounds are much more stable, and silanes with tertiary amino-groups are not decomposed on prolonged heat treatment up to 300°C, while those with secondary amino-groups eliminate ethylene at this temperature with a 30% yield[85]:



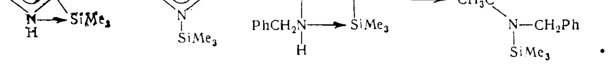
Quaternary salts decompose in the same way, but silylamines with alkoxy-groups at the silicon atom are stable.

Organosilicon derivatives of aldimines rearrange very slowly at room temperature to the corresponding *N*-derivatives[86]:

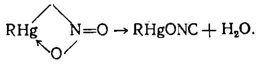


The isomerisation is sharply accelerated in the presence of 10 mole % of trimethylsilyl bromide and depends markedly on steric factors; for example, with R = t-Bu or iso-Pr there is no isomerisation. It is very probable that the non-catalysed rearrangement takes place intramolecularly, by analogy with the keto–enol isomerisation (see Section III).

Diatropic rearrangements with exchange of the trimethylsilyl group for hydrogen in 2-trimethylsilylpyrrole at room temperature[87] and in silylacetamidines at 95–200°C[88] apparently take place in the same way, although their mechanism has not been investigated (these rearrangements are considered in greater detail in Section III):



Kashutina and Okhlobystin[89] suggest that this is why α-nitromethyl derivatives of mercury decompose at the instant of formation to fulminate and water:

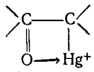


It is interesting to note that trinitromethyl compounds of mercury are fairly stable and it is believed[89] that the possibility of dehydration is a necessary condition for the rearrangement.

III. COMPLEXES WITH OXYGEN-SUBGROUP LIGANDS

1. Aldehydes and Ketones

The carbonyl group in α-carbonyl organic derivatives of the elements has "anomalous" spectroscopic properties compared with carbon analogues—its absorption in the infrared and ultraviolet spectra is displaced towards longer wavelengths and the band intensities are greatly enhanced. These findings have been explained by σ,π conjugation[90]. However, the even greater shift of the ν(CO) wavenumber (to 1645 cm^{-1}), while ν(CH) retains its normal value in the $RHgCH_2CHO$ (R = Cl or CH_2CHO) spectra would be difficult to understand in terms of conjugation, which led to the hypothesis[91] that both intramolecular and intermolecular CO → Hg coordinate bonds are formed in these compounds. The IAMC hypothesis, leading to a decrease of the positive charge on the metal, was put forward to explain the low rate constant for the electrochemical reduction of α-carbonyl derivatives of mercury[92]:



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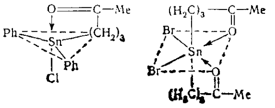
Attempts have been made in a number of studies to determine the main effect responsible for these anomalies. The increase of the intensity of the *n* → π* transition band by a factor of 4–5 in the spectra of α-silylketones compared with the carbon analogues confirmed, according to Musker and Ashby[93], the presence of a CO → Si intramolecular coordinate bond and could not be explained by steric and inductive effects. However, the exaltation of the *n* → π* transition is observed in many other ketones and may be due to factors which do not affect the absorption by the carbonyl group. The significant difference between the observed and calculated wavenumbers of the carbonyl group in the spectra of α-silylketones and their carbon analogues cannot serve as proof of a greater contribution by IAMC compared with the inductive effect of the trialkylsilyl group, since no account was taken in the calculations of the influence of the field and other factors which may be more important than the inductive effects[94]. Furthermore, it follows from the infrared spectra of α-silylketones in the gas phase [the bathochromic shift of ν(CO)][95] that there is no intermolecular coordination in these compounds.

There are probably concerted effects of the CO → Si intramolecular coordinate bond and the inductive effect of the R_2Si-group in α-silylketones, since the ν(CO) band in the spectrum of α-triphenylsilylcyclohexanone is split in carbon tetrachloride into two components, the intensities of which vary with temperature, but the splitting itself is independent of concentration and can therefore be accounted for by a conformational equilibrium[94]. Intramolecular coordination probably obtains also in α-stannylketones, since an appreciable quadrupole splitting (Δ) is observed in their Mössbauer spectra and furthermore such interaction is not inconsistent with mass-spectrometric data[10].

Coordination of this kind is absent from β- and γ-stannylketones[10,96] but becomes appreciable when the hydrocarbon groups at the tin atom in these compounds are replaced by powerful electronegative groups—halogens (see Table)[96].

The values of ν(CO) permit the existence of an Sn ← OC intramolecular coordinate bond in compounds (III), (IV), and (VII) but not in (II) and (V), since the tin atom in compounds of the latter type does not usually exhibit coordinating properties.

When complexes (IV), (VI), and (VII) with bipyridyl are formed, the intramolecular coordinate bond is ruptured and the ν(CO) wavenumbers become characteristic of the free carbonyl group. The occurrence of intramolecular coordination is confirmed also by the analysis of the chemical shifts of the protons in the methylene group linked to the carbonyl group. The signals of compounds (II) and (V) are located in the region of τ = 7.55 p.p.m. The replacement of the phenyl group by a halogen in these compounds causes their downfield shift in consequence of the appearance of IAMC, which reduces magnetic shielding. On the other hand, in the bipyridyl complexes (IV), (VI), and (VII) the carbonyl group is liberated and the proton signals again appear in the region of τ = 7.55 p.p.m. There is no intermolecular coordination in these compounds, since compounds (III) and (VII) are monomeric in benzene. There is no splitting Δ in the Mössbauer spectra of compounds (II) and (V), which is as a rule a characteristic feature of tetracoordinate organotin compounds, but it is appreciable in the spectra of compounds (III) and (VII). The magnitude and sign of Δ suggest the following structure of these compounds:



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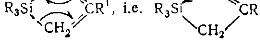
The occurrence of intramolecular or intermolecular coordination in non-reacting organic derivatives of the elements with α-carbonyl groups should facilitate the possible elementotropic rearrangements, since such interaction lowers the activation energy for the transition complex. Indeed α-silylketones rearrange to the isomeric siloxyalkenes on heating to 160–180°C for 2–3 h [97] or on standing in the presence of catalytic amounts of mercury and zinc salts and halogenosilanes[98]: $R_3SiCH_2COR' \rightarrow R_3SiOC(R') = CH_2$, where R and R′ = alkyl or aryl.

The thermal rearrangement is a process common to these compounds and takes place intramolecularly via a four-membered transition state[97]:



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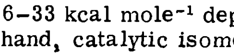
This is proved by the following findings: (a) the retention of configuration in the thermolysis of the optically active ketone (+)-α-(methylphenyl-1-naphthylsilyl)benzophenone[97]; (b) the absence of intermolecular interaction products in the thermolysis of a mixture of α-trimethylsilylacetophenone and triethylsilylacetone[98]; (c) the first order of the reaction[97]. The activation energy for the rearrangement is 26–33 kcal $mole^{-1}$ depending on R and R′.[99] On the other hand, catalytic isomerisation is an intermolecular process[98].

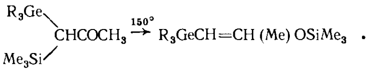
Silylmethyl sulphoxides, which are heteroanalogues of α-silylketones, undergo a remarkable rearrangement[100]:



$$Me_3SiCH_2\underset{\overset{\|}{O}}{S}R \xrightarrow{60°} Me_3SiOCH_2SR.$$

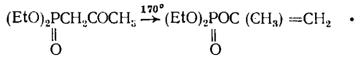
Its mechanism is obscure. The germanium analogue does not isomerise under these conditions and the phosphorus analogue $Me_3SiCH_2P(O)Ph_2$ is stable even at 180°C.

αα-Dimetallated ketones also isomerise on heating. Thus germyl silyl ketones are converted into *C*-silylated germyl-substituted enols[101] at a higher rate than α-monosilylketones:



$$\begin{matrix}\mathrm{R_3Ge}\diagdown & \\ & \mathrm{CHCOCH_3}\xrightarrow{150^\circ}\mathrm{R_3GeCH{=}CH(Me)OSiMe_3}\ . \\ \mathrm{Me_3Si}\diagup & \end{matrix}$$

A phosphonate ester rearranges similarly (to the extent of 50% in the presence of 2% orthophosphoric acid and to the extent of only 1% in the absence of a catalyst)[102]:



$$\underset{\mathrm{O}}{\overset{}{\mathrm{(EtO)_2\overset{}{P}}}}\mathrm{CH_2COCH_3}\xrightarrow{170^\circ}\underset{\mathrm{O}}{\mathrm{(EtO)_2P}}\mathrm{OC(CH_3){=}CH_2}\ .$$

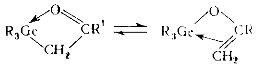
It is believed that the rearrangement proceeds intramolecularly, since it is unaffected by the addition of 2-butanone.

Spectroscopic properties of γ-stannylketones.[96]

Compound	ν(CO), cm^{-1} (in liq. paraffin)	τ_{CH_2CO}, p.p.m. (in $CDCl_3$)	δ for SnO_2, mm s^{-1}	Δ, mm s^{-1}
(II) $Ph_3Sn(CH_2)_3COMe$	1705	7,55	1.73	0
(III) $Ph_2ClSn(CH_2)_3COMe$	1669	7,46	1.38	−3.30
(IV) $PhCl_2Sn(CH_2)_3COMe$	1670	7,30	—	—
$PhCl_2Sn(CH_2)_3COMe\cdot$bipy *	1710	7.55	—	—
(V) $Ph_2Sn[(CH_2)_3COMe]_2$	1709	7,55	1,41	0
(VI) $Cl_2Sn[(CH_2)_3COMe]_2$	1680	7.23	—	—
$Cl_2Sn[(CH_2)_3COMe]_2\cdot$bipy	1705	7.42	—	—
(VII) $Br_2Sn[(CH_2)_3COMe]_2$	1675	7.27	1,66	+3.83
$Br_2Sn[(CH_2)_3COMe]_2\cdot$bipy	1703	7,55	1.56	+3.80

*bipy = 2,2′-bipyridyl.

True elementotropic tautomerism occurs in the case of α-germylketones[103], the equilibrium position depending strongly on temperature, an increase of which increases the content of the *O*-isomer. The equilibrium between the isomers is established slowly (in about one month)[104] at room temperature and much faster following the addition of bromogermanes. Presumably this reversible rearrangement proceeds via a coordination complex:

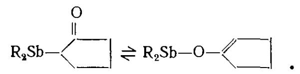


The contents of the *C*- and *O*-isomers depend strongly on the substituent linked to the keto-group. Thus, at 20°C and with R = CH_3, the equilibrium mixture contains 3% of the *O*-isomer for R′ = CH_3 [105] and 33.7% for R′ = *p*-ClC_6H_4.[106] The germanotropic equilibrium constant is satisfactorily correlated with Hammett's σ constant (ρ = 1.67). Consequently electron-donating substituents in the aromatic ring decrease and electron-accepting substituents increase the concentration of the *O*-isomer in the equilibrium mixture, which occurs in prototropic keto–enol systems, but in a series of organic derivatives of the elements, this influence is much stronger. The thermodynamic parameters of the isomerisation reaction have been calculated from the temperature variation of the equilibrium constants; for example $\Delta H = 2.64 \pm 0.05$ kcal mole^{-1} and $\Delta S = 2.1 \pm 0.1$ kcal mole^{-1} K^{-1} for R = R′ = CH_3.[106] Fractionation of the mixture of isomers can displace the equilibrium almost completely towards the more volatile *O*-isomer.

Stannylmethyl ketones and the corresponding *O*-stannylenols undergo interconversions at much higher rates than their germanium analogues. The rearrangement is also reversible but proceeds intermolecularly[105,107] and is greatly accelerated following the addition of trialkyltin halides (the average lifetime of the isomers is 10^{-1}–10^{-3} s). Depending on the substituents R and R′, the equilibrium mixture may contain 6–23% of the *O*-isomers, the amount of which is frequently independent of temperature.

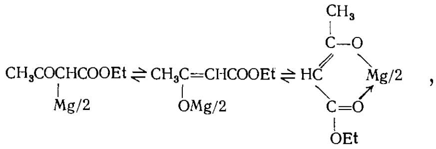
$$\mathrm{R_3SnCH_2COR'} \rightleftharpoons \mathrm{R_3SnOC(R')C{=}CH_2}\ .$$

In the series of similar antimony compounds, the rate of equilibration depends on the structure of the ketone. In the antimony derivatives of cyclohexanone, the rate is approximately the same as for stannylmethyl ketones, while the cyclopentanone compound of antimony isomerises much more slowly. With increase of temperature, the content of the *O*-isomer in the equilibrium mixture rises: for example from 20% at 20°C to 30% at 113°C for the latter compound[108]:

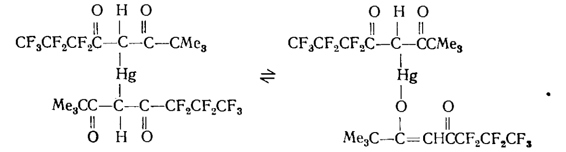


The mechanism of this rearrangement is unknown.

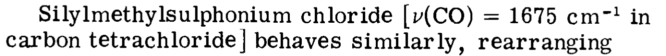
Keto-enol tautomerism probably occurs in the magnesium derivatives of acetoacetic ester, the infrared spectra of which depend markedly on the solvent and concentration[109]:



and also in the mercury derivatives of β-diketones (two different constants $J_{^1H-C-^{199}Hg}$ have been obtained in acetone at −75°C, namely 257 and 273 Hz):[110]

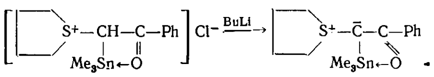


It is believed that the interaction of trialkylsilylketens with trialkyl phosphites and phosphorothioites (X = O or S) proceeds via intermediate ketophosphinate esters, which then isomerise intramolecularly to the corresponding siloxyvinyl compounds with 70–85% yields[111]:

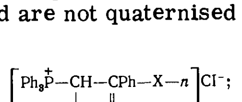


Silylmethylsulphonium chloride [ν(CO) = 1675 cm^{-1} in carbon tetrachloride] behaves similarly, rearranging slowly to siloxyvinyl sulphide at room temperature[112]:

The tin analogue is stable, but the marked decrease of ν(CO) (to 1524 and 1487 cm^{-1} in KBr) suggests the existence of an $\mathrm{Sn} \leftarrow \mathrm{OC}\langle$ intramolecular coordinate linkage in this compound. When it is acted upon by butyl-lithium in THF, butane is evolved: the former coordination is probably regained in the resulting ylid $[\nu(\mathrm{CO}) = 1528\ \mathrm{cm^{-1}}]$[112]:



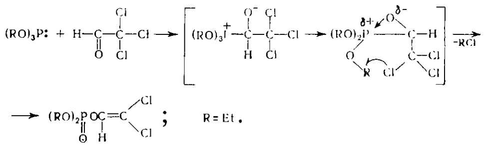
The same type of interaction has been suggested also for phosphoranes $[\nu(\mathrm{CO}) = 1470{-}1495\ \mathrm{cm^{-1}}$ in KBr]. Furthermore, these compounds are resistant to hydrolysis and methanolysis and are not quaternised by methyl iodide[113].



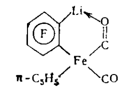
$$\left[\mathrm{Ph_3\overset{+}{P}{-}\underset{\underset{R_3Sn\leftarrow}{|}}{CH}{-}\underset{\underset{O}{\|}}{C}Ph{-}X{-}}n\right]\mathrm{Cl^-};$$

X=H, Me, OMe, Cl, Br.

A remarkable example of the influence of the possible intramolecular coordination on reactivity is the Perkow reaction—the interaction of triethyl phosphite with chloral to form ββ-dichlorovinyl diethyl phosphate. According to one of the proposed mechanisms, the reaction proceeds via phosphonium salts[114]:

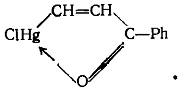


Intramolecular coordination is the cause of the unusually high stability of complex (VIII)[115]:



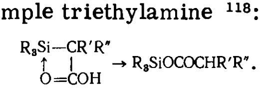
ortho-Fluorolithio-derivatives of aromatic compounds are known to be thermally unstable and to form arynes readily[3]. However the corresponding aryne has not been observed (the Diels-Alder reaction with furan leads to the *ortho*-hydrotetrafluorophenyl derivative in quantitative yield) for compound (VIII) (containing an iron atom in the *ortho*-position), while the *meta*- and *para*-isomers give rise to the normal addition products. A similar difference has been observed also between the exchange reactions involving $(\pi\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{FeI}$. The coordination in this compound breaks down following the addition of $\mathrm{D_2O}$ (the *o*-deutero-isomer has been isolated quantitatively).

The higher stability of *cis*-β-oxovinylmercury halides compared with the *trans*-analogues has been explained similarly[116]. X-Ray diffraction analysis of *cis*-β-benzoylvinylmercury chloride demonstrated a cisoid conformation of the molecule in which the oxygen atom is directed towards the mercury atom (R = 13.6%; $l_{\mathrm{Hg...O}} = 2.88$ Å). The Hg...O distance and the sum of the van der Waals radii (2.9–3.1 Å) are within the limits of experimental accuracy. However, the decrease of the ClHgC angle, located opposite the oxygen atom, to 173° ± 2° and the conformation of the molecule suggest the following coordination[117]:



2. Acids and Their Derivatives

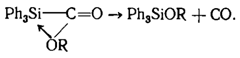
Silylacetic acids rearrange to the isomeric acyloxysilanes at the melting point and also under very mild conditions, frequently at 25°C, in the presence of basic catalysts, for example triethylamine [118]:



$$\mathrm{\underset{\underset{O=}{\uparrow}}{R_3Si}{-}\underset{\underset{COH}{|}}{C}R'R''\rightarrow R_3SiOCOCHR'R''}.$$

The thermal isomerisation proceeds intermolecularly while the catalytic isomerisation can be both intermolecular and intramolecular. However, in highly dilute solutions, where the extent of bimolecular reactions is reduced to a minimum, only the intramolecular pathway operates, since optically active vinylacetic acids are converted into the corresponding acetoxysilanes with retention of configuration at the silicon atom[119].

Silyl derivatives of carboxylic acids and their esters are readily decarboxylated at 150–230°C via an intramolecular mechanism, which has been demonstrated by kinetic data and also by the finding that the thermolysis of a mixture of the esters does not lead to intermolecular interaction products[99]:

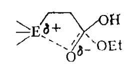


The ester of stannylated phenylacetic acid reacts with $\mathrm{SiCl_4}$ to form a keten acetal, which readily isomerises in 2–3 days at room temperature to the carbon derivative until the attainment of equilibrium[120]:

$$\mathrm{R_3SiCH(Ph)COOMe\xrightarrow{SiCl_4}\underset{5\%}{PhCH{=}C(OMe)OSiCl_3}\rightleftharpoons\underset{95\%}{Cl_3SiCH(Ph)COOMe}}.$$

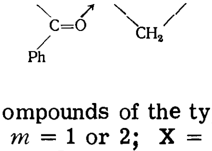
This is the first instance of silylotropism. Distillation of the equilibrium mixture leads to a slight shift of equilibrium towards the *O*-isomer, but the initial equilibrium position is restored after the period stated above.

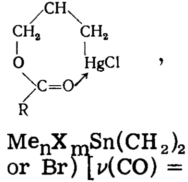
The esters $\mathrm{Et_3E(CH_2)_2COOEt}$ (E = Si, Ge, or Sn) hydrolyse much faster than ethyl butyrate or $\mathrm{Et_3E(CH_2)_3.COOEt}$, which cannot be accounted for solely by the inductive effect of the $\mathrm{Et_3E}$ groups. It is believed[121] that the higher rate of hydrolysis can be explained by the formation of intermediate complexes:



Such stabilisation of the transition state is absent for $\mathrm{Et_3Sn(CH_2)_3COOEt}$, since five-membered rings are frequently formed at a higher rate than six-membered rings.

In view of the reduced values of ν(CO), intramolecular coordination has been suggested for bis(benzoyloxymethyl)zinc $[\nu(\mathrm{CO}) = 1645\ \mathrm{cm^{-1}}]$ [122] and carboxypropyl derivatives of mercury $[\nu(\mathrm{CO}) = 1680{-}1710\ \mathrm{cm^{-1}}]$ [123]:





and also in compounds of the type $\mathrm{Me}_n\mathrm{X}_m\mathrm{Sn(CH_2)_2COOMe}$ (n = 1 or 2; m = 1 or 2; X = Cl or Br) $[\nu(\mathrm{CO}) = 1656$ to $1680\ \mathrm{cm^{-1}}$ in KBr] [124], the τ_{MeO} signal in the ^{1}H NMR spectra of which undergoes a downfield shift. It is suggested that a trigonal bypyramidal structure occurs in these compounds, one of its vertices being occupied by the acetoxy-group[124].

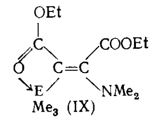
It is noteworthy that intramolecular coordination occurs in R_3SnCH_2COOMe but not in R_3SnCH_2OCOMe (according to Mössbauer spectra)[95], which is probably associated with the greater inductive effect of the methoxycarbonyl group compared with the acetoxy-group.

Internal coordination has been suggested also for diazoesters:

$$R_{4-n}Sn\,[C(N_2)COOEt]_n \text{ (where } n=1,2) \text{ and } YC(N_2)COOEt\ ,$$

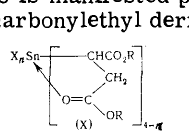
where Y = Me_3Si, Me_3Ge, Me_3Pb, or RHg, in view of the high dipole moment $\mu = 2.2$ D (for $n = 1$ and R = Me), the monomeric state of the compounds in benzene (for tin compounds), and the appreciably reduced values of ν(CO) (1640–1675 cm^{-1}) and ν(N≡N) (2045–2070 cm^{-1}) compared with the carbon analogues[125]. The coordination in diazoesters is probably stronger than in α-ketones and α-carboxyesters, since the shift of ν(CO) in the latter compounds is smaller.

The occurrence of intramolecular coordination is the cause of the splitting of the ν(CO) bands (1735 and 1680 cm^{-1} for E = Si, 1739 and 1698 cm^{-1} for E = Ge, and 1740 and 1705 cm^{-1} for E = Sn) and ν(C=C) bands (1570 and 1550 cm^{-1} for E = Si, 1590 and 1555 cm^{-1} for E = Ge, and 1625 and 1590 cm^{-1} for E = Sn) in the infrared spectra of compounds of type (IX)[126] (see also Riviera-Boudet and Satge[127]):



(IX)

The difference between the coordinated and covalently linked carbonyl groups is manifested particularly clearly in organotin diethoxycarbonylethyl derivatives (X),



(X)

X = Hal; n = 2, 3

the spectra of which contain ν(CO) bands in the ranges 1634–1660 and 1692–1718 cm^{-1}.[128,129] A trigonal bipyramid with the ethoxycarbonyl group at one of the vertices has been proposed for n = 3.[129] Two isomers have been isolated for n = 2 and X = Br and their crystal structures have been determined[130,131]. They both (R = 9.8 and 16.7%) have distorted octahedral structures. The two bromine atoms are in the *cis*-positions and the 1,2-di(ethoxycarbonyl)ethyl groups are linked to the tin atom via oxygen and carbon atoms with formation of five-membered rings. The Sn–O bond length (2.44–2.49 Å) greatly exceeds the sum of the covalent radii (2.06 Å) and the Sn ← OC coordination is therefore fairly weak.

In consequence of amide conjugation, the organic acid amide derivatives of the elements are much more labile than the corresponding α-ketones and α-acids and therefore rearrange under more severe conditions[132–134]; secondary amides rearrange to the N-isomers, while acylated N-alkylamides rearrange to the O-isomers. These isomerisations probably also proceed via an intramolecular mechanism:

$$R_3ECH_2CONHR' \xrightarrow{140-200°} R_3EN(R')COCH_3; \text{ E = Si, Ge,}$$

$$Et_3SiCH_2CON(Me)COR \xrightarrow{160-180°} Et_3SiOC[N(Me)COR]{=}CH_2.$$

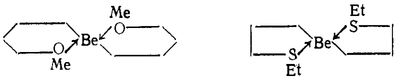
It is believed that intermediates with intramolecular coordination of the type

are formed in the hydroboration of N-alkenylureas and N-alkenylcarbamates, which reduces the reactivity of H_2B groups, prevents further hydroboration, and after hydrolysis leads to high yields of the corresponding alkylboronic acids, while in the case of terminal olefins trialkylboron compounds are formed exclusively[135].

3. Alcohols and Ethers

Alcohol and ether derivatives of the elements frequently exhibit reduced thermal stability as a result of O → E intermolecular coordination and evolve comparatively readily ethylene and cyclopropane (CP) or their derivatives, particularly in those cases where the functional group is in the β- and γ-positions with respect to the element. Such ready β- and γ-elimination is undoubtedly associated with the higher strength (energy) of E–O bonds compared with E–C bonds. In some cases such compounds could be isolated under mild conditions.

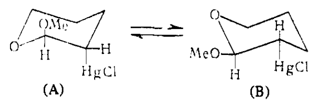
The stability of di-(δ-methoxybutyl)- and di-(γ-ethylthiopropyl)-beryllium on distillation in a high vacuum suggested that these compounds exist as inner-complex salts[136]:



In solutions *cis*-β-mercurated alicyclic alcohols are probably also involved in intramolecular coordination, since the OH absorption band in the infrared spectra is displaced towards longer wavelengths by 18–22 cm^{-1} compared with the carbon analogues[137], while the shift for the *trans*-isomers is only 6–10 cm^{-1}. However, it is not altogether clear whether this approach can be used for open-chain compounds or compounds with conformationally mobile rings. The study of the conformation equilibria of the mercury derivatives of tetrahydropyran in acetonitrile,

$$(A) \rightleftharpoons (B)$$

showed that the strength of the coordinate bond in these compounds is low[138]. It has been found from ^1H NMR spectra that the equilibrium mixture contains at least 56% of conformation (B) (ΔG = −0.14 kcal $mole^{-1}$):

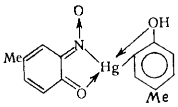


Since ΔG for HgX groups is equal or close to zero, intramolecular coordination stabilises conformation (B) with an energy of about 1 kcal $mole^{-1}$. It has been suggested[138] that the intramolecular stabilisation of unstable conformations is common to all compounds with substituents between which appreciable coordination interaction is possible.

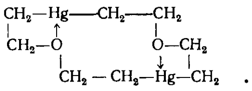
This conclusion was confirmed in a study of the dipole moments of β-substituted mercury compounds of the type $HalHgCH_2CH_2X$ [Hal = Cl, Br, or I; X = OMe, OCOMe, CF_3, or $C(NO_2)_3$].[139] In the series of these compounds, intramolecular coordination occurs in benzene only for X = OMe or OCOMe and in the former case is so weak that it breaks down following the addition of ethyl acetate. The capacity for intramolecular coordination decreases in the following sequence of substituents X: MeOCO > MeO ≫ CF_3 > $C(NO_2)_3$. For the last two substituents, this conclusion had been made earlier on the grounds that, when these compounds are acted upon by nucleophiles, ethylene is not evolved owing to the absence of electron-donating groups capable of coordination, while the presence in the β-position of substituents with an unshared electron pair (OR, OCOR, and NR_2) leads under the same conditions to complete β-elimination. Furthermore, when X = CF_3, the constant $J_{(CF_3...Hg)}$ for the ^{19}F NMR spectrum in carbon tetrachloride is extremely low[140, 141].

However, in the crystalline state there is no intramolecular coordination at all in the mercury compounds, which has been shown convincingly by X-ray diffraction. Thus the mutual orientation of the substituents relative to the cyclohexane ring in the α(*dd*, *ll*) and β(*dl*, *dl*) diastereoisomers of 2-methoxycyclohexylmercury chloride proved to be different, the intramolecular Hg...O distances in the α-isomer (4.06 Å) and in the β-isomer (3.06 Å) virtually ruling out intramolecular coordination[142].

The Hg...O distance in the 2-hydroxy-5-methylphenylmercury derivative of 5-methylnitrosophenol is 3.00 Å, the C–N and N–O linkages are close to double bonds, and the mercury atom is joined covalently to the carbon atoms of the phenolic ring and the nitrogen atom of benzoquinone (*R* = 11%).[143] However, in this case the very weak Hg ← O interaction is largely determined by the rigidity of the molecular geometry:

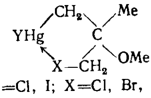


Hg ← N intermolecular coordination (2.77 Å) with almost planar conformation of the –Hg–C–C–N group (*R* = 5.6%) obtains even in *N*-[2-(chloromercuri)ethyl]-diethylamine[144]. An exception is the dimeric molecule of ββ'-oxidodiethylmercury[145]:



Here intramolecular coordination leads to the formation of a tricyclic structure (l_{HgO} = 2.21 ± 0.06 Å). However, following a slight decrease of the CHgC angle (to 176°), the hybrisation of the mercury atom remains virtually unchanged, which indicates a low accuracy of the above investigation.

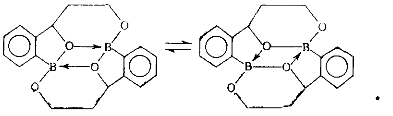
When organomercury compounds contain an atom with a free electron pair in both β- and γ-positions, intramolecular coordination occurs with formation of a five-membered ring in consequence of smaller angular strain. This is the cause of the non-equivalence of the methylene protons in the ^1H NMR spectra of compound (XI):



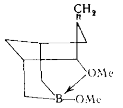
Y=Cl, I; X=Cl, Br, OH.
(XI)

[Y = Cl; X = Cl or Br; $\Delta\nu(CH_2Br)$ = 19.1 Hz; $\Delta\nu(CH_2Hg)$ = 13.6 Hz]; the non-equivalence diminishes sharply in the presence of solvents which break the coordinate bond, for example pyridine, and this leads in its turn to a decrease of J_{HgCCCH_3} (it amounts to 36 Hz in $CDCl_3$ and 20 Hz in pyridine)[146]. When Y = I and X = OH, a temperature variation of J_{HCOH} is observed in $CDCl_3$ and ν(OH) in the infrared spectrum falls to 3584 cm^{-1}.[147] The non-equivalence of the methylene protons in compounds of the type $BrHgCH_2CR(OR')COX$ (R = Me, Ph, OBu-t, or Me and X = Me or OMe) is even more pronounced [$\nu(CH_2Hg)$ = 8.7–29.7 Hz in carbon tetrachloride]. However, it is difficult to determine in this instance which oxygen atom is involved in the Hg ← O intramolecular coordination: peroxide, carbonyl, or ester oxygen[148].

Internal coordination is responsible for the enhanced hydrolytic and chemical stability (there is no reaction with 2-aminoethanol and *o*-phenylenediamine under mild conditions) of the boronate diester[149]:



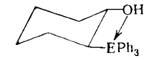
The doublet of signals in the ^{11}B NMR spectrum (with chemical shifts of –30.5 and –51.3 p.p.m. relative to $Et_2O.BF_3$) corresponds to the coordinated and free boron atoms in the bicyclic ester (XII),



(XII)

which evidently exists in the form of an equilibrium mixture of chair-boat and chair-chair conformers, the proportions of which have been found to be 65 : 35.[150]

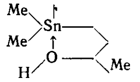
The enhanced acidity of silyl (germyl)-substituted cyclohexanols (XIII)



(XIII)
(E = Si, Ge)

relative to carbon analogues, which has been established on the basis of the large shifts of the ν(OH) bands in the infrared spectra following the addition of DMSO and THF, can be accounted for by E ← O intramolecular coordination, since the electropositive influence of silicon and germanium should reduce the acidity of these alcohols[94]. On the other hand, the acidity of 1,1,1-triphenylethanol derivatives of silicon and germanium is normal[151]. The large difference clearly demonstrates the influence of conformation on the proximity of the electron-donating and electron-accepting atoms.

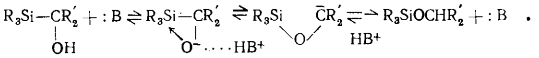
The coordination in γ-stannylethanol (XIV)



(XIV)

probably takes place as a result of the very high value of $J_{^{117}/^{119}Sn\text{-}CH_3}$ in the ^1H NMR spectrum, which amounts to 60.6/63.4 Hz in 0.32 M solution in carbon tetrachloride in the presence of added tris(dipivaloylmethanato)europium[152].

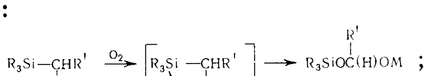
In the presence of basic catalysts (active metals, organometallic compounds, or amines), silylmethanols readily rearrange to alkoxysilanes[153-156] via a pseudo-first-order reaction[157]. Its rate is very sensitive to the nature of the group at the methanol centre and the activation energy is 8–11 kcal $mole^{-1}$. The basic catalyst removes the acid proton and the resulting α-hydroxy-ion then undergoes an intramolecular rearrangement with formation of a stronger Si–O bond and the fixation of the negative charge at the carbon atom. The carbanion formed is rapidly protonated to alkoxysilane:



$$R_3Si-\underset{\underset{OH}{|}}{C}R'_2 + :B \rightleftharpoons R_3Si-\underset{O^-\cdots HB^+}{C}R'_2 \rightleftharpoons R_3Si\underset{O}{\quad}\bar{C}R'_2 \underset{HB^+}{\rightleftharpoons} R_3SiOCHR'_2 + :B\ .$$

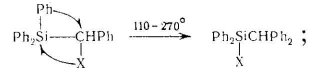
This isomerisation proceeds with retention of configuration at the chiral Si centre[158] and with its inversion at the chiral carbinol centre[159].

The products of the oxidation of the Si–C bond in α-trialkylsilyl organometallic compounds, i.e. hydroperoxy-salts[160], undergo a similar rearrangement and are converted as a result of hydrolysis into silanols and siloxanes:



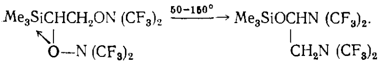
$$R_3Si-\underset{\underset{M}{|}}{C}HR' \xrightarrow{O_2} \left[R_3Si-\underset{\underset{OOM}{|}}{C}HR'\right] \longrightarrow R_3SiO\overset{\overset{R'}{|}}{C}(H)OM\ ;\quad M = MgCl,\ AlBu_2\ .$$

The thermal rearrangements of α-substituted benzyltriphenylsilanes probably proceed via an intramolecular mechanism with migration of the substituent X to the silicon atom accompanied by the transfer of the phenyl group from silicon to carbon[161]:



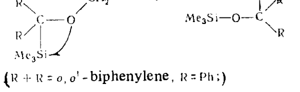
X = OAc, OTs, F, Cl .

This also happens in the thermal rearrangement of trifluoromethylaminoxyalkylsilanes with dissociation of the Si–C and N–O bonds and the formation of stronger Si–O and N–C bonds[162]:



$$Me_3Si\underset{\underset{O-N(CF_3)_2}{|}}{C}HCH_2ON(CF_3)_2 \xrightarrow{50-150^\circ} Me_3SiO\underset{\underset{CH_2N(CF_3)_2}{|}}{C}HN(CF_3)_2.$$

These isomerisations, which take place almost quantitatively (the latter is a first-order reaction), are examples of diatropic rearrangements in which two σ bonds change places as a result of the cyclic process. A study of the kinetics of the conversion of allyl silylmethyl ether to a silylether[163]

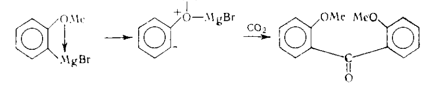


(R + R = o,o'-biphenylene, R = Ph;)

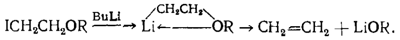
showed that the rearrangement does not proceed via a single mechanism. For example, when R + R = oo'-biphenylene, the silyl group migrates intramolecularly to the extent of 100%, while the allyl group migrates via this mechanism only to the extent of 72%. The isomerisation proceed via a first-order reaction and depends only slightly on the solvent. The activation parameters (in benzene) are $E_a = 32.3 \pm 0.6$ kcal $mole^{-1}$, $\Delta H^{\neq} = 31.4 \pm 0.6$ kcal $mole^{-1}$, and $\Delta S^{\neq} = -8.9 \pm 0.8$ cal K^{-1}.

β-Metallated alcohols and ethers are fairly stable in solution in aromatic compounds. Like aminoferrocenes (aminobenzenes), alkoxyferrocenes (alkoxybenzenes) are therefore metallated by butyl-lithium only at the site adjoining the substituent owing to Li ← OR intramolecular coordination, benzene derivatives reacting much more slowly. Substituted ferrocenes with X = CPh_2OH,[164] OMe,[165,166] CH_2OR,[167] or Cl[166] and benzenes with X = OMe[168] or SO_2CMe_3[169] have been used. In the case of thioanisole[170], the α-position of the ring is metallated with subsequent transfer of the lithium atom to the methyl group, probably as a result of *trans*-metallation.

Internal coordination has also been proposed to account for the anomalous reactions between CO_2 and Grignard reagents derived from o-bromomethoxy(methylthio-, dimethylamino-)benzenes, as a result of which both acids and ketones have been obtained[171-173]. The formation of the latter can be understood on the basis of this scheme

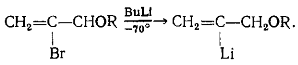


Aliphatic β-lithioethers very readily eliminate lithium alkoxides owing to the Li ← OR intramolecular coordination and can therefore be obtained only at very low temperatures[174,175]. For example, when β-iodoethers are acted upon by butyl-lithium, the main product is ethylene with only a 5% yield of the desired product[174]:



$$ICH_2CH_2OR \xrightarrow{BuLi} Li\overset{CH_2CH_2}{\longleftarrow}OR \rightarrow CH_2{=}CH_2 + LiOR.$$

Similar α-vinyl-lithium compounds are much more stable and can be obtained in a preparative yield, for example[176,177]:



$$CH_2{=}\underset{\underset{Br}{|}}{C}-CHOR \xrightarrow[-70^\circ]{BuLi} CH_2{=}\underset{\underset{Li}{|}}{C}-CH_2OR.$$

β-Alkoxyethylmagnesium compounds are extremely unstable (see Section II).

It is interesting to note that ethers [and sulphides] of the type $ROCH_2MgCl$ and $PhCH_2SCH_2MgCl$ are stable at −30° and 0°C respectively, but [at higher temperatures?] decompose with elimination of ethylene[178]:

$$2ROCH_2MgCl \rightarrow CH_2{=}CH_2 + 2ROMgCl.$$

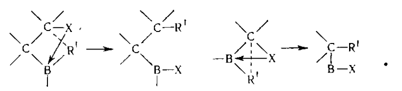
However, in the presence of cyclohexene their decomposition does not lead to the formation of norcarane[178], so that the elimination of ethylene most probably proceeds via intermolecular coordination.

β-Alkoxyethyl derivatives of boron are also thermally unstable. For example, tris-(2-alkoxyethyl)boron begins to evolve ethylene at a temperature as low as −10°C. However, the stability of these compounds increases as the 2-alkoxyethyl groups are substituted by alkoxy-groups and 2-alkoxydiethoxyboron decomposes only at 160–170°C.[179]

It has been shown that the ease of elimination of olefins from the compounds $R_2B\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}X$ depends on X. When X = OTs, OBz, OAc, or Cl, the decomposition takes place below 0°C, while for X = OAlk(Ar) the compound can be isolated[180,181].

It has been shown for deuterated[182] and cyclohexane[183] derivatives of boron that thermal β-elimination takes place via an intramolecular mechanism. Under comparable conditions, β-alkoxylethylboron compounds form olefins more readily than the analogous sulphur derivatives[182,184].

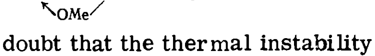
β-Elimination may be accompanied also by a β-transition (a new type of diatropic rearrangement), which likewise proceeds intramolecularly[185,186]. α-Transition reactions proceed similarly[183,185]:



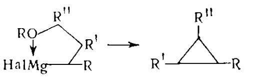
X = OR, SR.

Al ← OR intramolecular coordination is probably the cause of the thermal instability also of β-alkoxyethyl derivatives of aluminium[33,187].

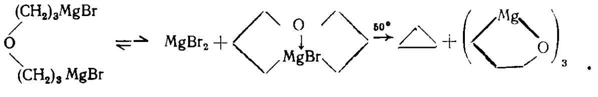
Similar silicon compounds decompose only under severe conditions and eliminate olefins quantitatively via a first-order reaction[188] (see also Tsurugi et al.[189]), for example:



There is no doubt that the thermal instability of 3-alkoxy(aryloxy)-derivatives of Grignard reagents can be accounted for by Mg ← OR intramolecular coordination[190–193]. This reaction can serve as a preparative method for the preparation of substituted cyclopropanes (yield of about 50%):

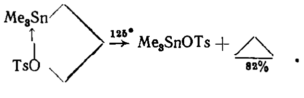


Bifunctional Grignard reagents disproportionate fully in THF into cyclic monomeric compounds (their degrees of association have been determined), which eliminate cyclopropane on thermolysis[194]:



On thermolysis, the compounds iso-$Bu_2Al(CH_2)_2OR$ (n = 3 or 4) form cyclopropane[34,195,196] and cyclobutane[34] respectively.

Tin compounds $Me_3Sn(CH_2)_nOTs$ ($n = 3$ or 4) behave in different ways depending on the value of n.[197] When $n = 3$, the thermolysis leads to cyclopropane, while in the case of n = 4–6 olefins are mainly produced, although 10% of cyclopentane has been obtained for $n = 5$:

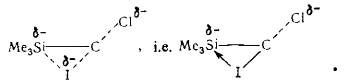


Presumably compounds of the type $E(CH_2)_nOR$ ($n > 3$) do not form cyclic products on thermolysis even when they contain reactive metals. For example, γ-ethoxybutylmagnesium bromide decomposes only with elimination of butyl ethyl ether[191].

IV. COMPLEXES WITH HALIDE LIGANDS

The extensive employment of many types of alkyl (aryl) halides and their derivatives in direct metallation reaction has led to the synthesis of numerous classes of organic derivatives of the elements with possible Hal – M intramolecular coordination and in the case of reactive metals most of them are extremely unstable at room temperature and readily decompose as a result of α- and β-elimination with formation of carbenes and arynes respectively[3]. In this part of the review we shall consider only compounds where intramolecular coordination is postulated in a non-reacting molecule, the transition state, or in thermolysis with formation of olefins and cycloalkanes.

Such coordination was postulated for the first time in the transition state to account for the sharp acceleration of the exchange (by a factor of 13) of the chlorine atom in trialkylchloromethylsilanes for an iodine atom in dry acetone (the Finkelstein reaction) in relation to the carbon analogues[198,199]:



This concept was subsequently used to explain the unusually easy nucleophilic substitution of the chlorine atom for I, OR, and SR in α-chloromethyl derivatives of mercury (the exchange is accelerated by a factor of 10^6 compared with n-BuCl)[200], boron[201], germanium, and tin[202]. It is noteworthy that there is no intramolecular coordination of this type in a non-reacting molecule (see Section I).

When alkyl substituents at the central atom are replaced by powerful electronegative groups capable of exciting the vacant orbitals of the central atom, intramolecular coordination takes place, as shown for trichloromethyl derivatives of mercury Cl_3CHgX (X = Cl, Br, or CCl_3). In ^{35}Cl NQR spectra there is appreciable (>2%) splitting of the lines due to the chlorine atoms in the CCl_3 group, which has been explained by an intramolecular interaction of one of the chlorine atoms with the mercury atom[203]. The authors believe[203] that such coordination has been confirmed by the X-ray diffraction analysis of Cl_3CHgBr in which Hg...Cl distances proved to be different—two of them are 3.21 Å and one is 3.15 Å. However, since the difference is within the limits of experimental error, the above conclusion cannot be regarded as reliable. Coordination in the above compounds breaks down when dimethoxyethane is added (the pronounced line splitting disappears), but not in the presence of ether[204].

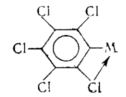
Cl → Sn intermolecular coordination probably also occurs in chloromethyltrichlorotin. Thus its mass spectrum[205] reveals the presence of rearranged fragments formed as a result of the ejection of carbene via a three-membered transition state, while the ^{35}Cl NQR spectrum of the $SnCl_3$ group[206] was found to consist of two lines with an intensity ratio of 1 : 2 and a splitting of about 6%, which exceeds by a factor of three the maximum possible crystallographic splitting. The non-equivalence of chlorine atoms has been explained by the possible coordination interaction between chlorine and tin, which can be both intermolecular and intramolecular. Cryoscopic determination of the molecular weight in benzene showed that there is no association. Furthermore, on reaction with an excess of relatively weak electron donors such as ether and benzene, the compound forms 1 : 1 (and not 1 : 2) complexes, existing only in solution (according to ^{35}Cl NQR spectra), which is not a characteristic feature of organotin compounds with powerful electronegative groups. This shows that the intramolecular coordination is stronger than the intermolecular coordination with ether and benzene. It was therefore assumed that these complexes have the configuration of a trigonal bipyramid with the tin atom in the centre and the three chlorine atoms in the equatorial plane; one of the vertices is occupied by the chlorine atom of the chloromethyl group and the other by a molecule of ether or benzene[2].

Ethyl acetate causes only a partial breakdown coordination in Cl_3SnCH_2Cl (according to dipole moment measurements), while pyridine destroys it completely with formation of a 1 : 2 complex; calorimetric data made it possible to estimate the energy of the intermolecular coordination as approximately 5 kcal mole^{-1}, which is typical for a hydrogen bond[13].

Finally, electron diffraction study of this compound in the vapour phase (R = 12.3%)[207] showed that its molecule is a distorted octahedron with hindered rotation about the Sn–C bond. However, one cannot conclude directly from these data that the Cl → Sn intramolecular coordinate bond is present.

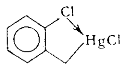
It is interesting to note that dichlorobis(chloromethyl)tin consists in the crystalline state of infinite chains with intermolecular Sn ← Cl bonds (X-ray diffraction analysis, R = 17.7%).[208]

The pentachlorophenyl derivatives of the number of metals have anomalous spectroscopic properties, which suggested the occurrence of intermolecular coordination:



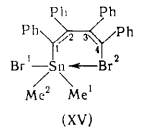
The compound with M = HgC_6Cl_5 melts at a much higher temperature than the corresponding pentafluorophenyl derivative[209]. The splitting of the frequencies of the *ortho*-chlorine atoms and their appreciable shift relative to the *meta*- and *para*-atoms have been observed in the ^{35}Cl NQR spectrum. The same characteristics have been found also for M = HgR (R = Cl, Me, or Ph).[210] Furthermore, low electrochemical reduction rate constants have been obtained for these compounds[92]. According to ultraviolet spectroscopic data, the pentafluorophenyl derivatives of silicon and tin have $\lambda_{max} \simeq 200$ nm, and a much higher molar absorption than their hydrogen-containing analogues[211]. *o*-Halogenophenyl derivatives of alkali and alkaline earth metals are extremely unstable owing to intramolecular coordination and the ease of formation of arynes, which is of great importance for synthesis[3]. The corresponding ferrocene derivatives are entirely stable (see Section III).

The absorption band corresponding to the vibrations of the Hg–Cl bond in the infrared spectrum of *o*-chlorobenzylmercury chloride is split into three components owing to the existence of several rotational isomers. The most intense component at 314 cm^{-1} has been attributed to the conformation with possible intramolecular coordination[212]:



A very interesting variation of the influence of substituents on intramolecular coordination has been observed in butadienyltin derivatives[213]. A doublet of equally intense signals due to the methyl protons (δ = 0.48 and 0.98 p.p.m., 36°C), merging into a singlet on heating to 87°C, has been found in the ^{1}H NMR spectrum of 4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-buta-1,3-dienyldimethyltin bromide (XV). The addition of basic solvents, for example ether or pyridine, has a similar influence. To explain the non-equivalence of the methyl protons in the diene, Sn ← Br intramolecular coordination was postulated: it stabilises the non-planar distorted cisoid conformation and hinders the rotation about the $C_{(2)}-C_{(3)}$ bond with a barrier of 18.3 ± 0.23 kcal mole^{-1} (according to ^{1}H NMR spectra) at room temperature and in non-basic solvents. Consequently intramolecular coordination can be disrupted by heating the specimen or by adding basic solvents.

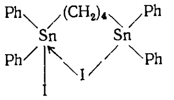
The proposed conformation of the diene (XV) in solution proved to be the same as in the crystalline state, as shown by X-ray diffraction (R = 10.7%).[213,214] The Sn ← Br bond length is 3.77 Å, which is smaller by 0.4 Å than the sum of the van der Waals radii of tin and bromine atoms. To ensure such coordination, the $C_{(1)}$–Sn–Me^1 angle has increased to 129° (from the tetrahedral angle of 109.5°) and the torsional angle in the butadiene fragment has increased to 68.1°:



(XV)

The introduction of the phenyl group in place of bromine and tin atoms should cause the breakdown of intramolecular coordination, since a tin atom linked to four carbon atoms does not usually exhibit coordinating properties. X-Ray diffraction analysis of this compound[215] confirmed this hypothesis: the Sn ← Br bond length is 4.346 Å and the $C_{(1)}$–Sn–Me^1 angle is 117.1°.

The conformation of the molecule can be very different in the crystalline state and in solution. For example, 1,4-bis(iododiphenylstannyl)butane has a high dipole moment in benzene (5.24 D), which is believed[216] to be associated with the existence of the inner complex (XVI):

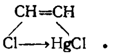


(XVI)

However, in the crystalline state the molecule proved to be symmetrical with a tetrahedral configuration of the tin atom (X-ray diffraction analysis; R = 9.6%).[217] At the same time, when iodine in compound (XVI) is replaced by hydroxy- and acetoxy-groups, the compounds probably exist in the crystalline state as inner complexes—their Mössbauer spectra show appreciable quadrupole splittings compared with the iodine analogue and the tin atom is undoubtedly pentacoordinate[218].

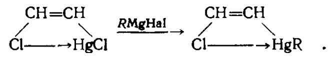
The influence of intramolecular coordination on the physical and chemical properties of organic derivatives of the elements has been studied in particularly great detail in relation to *cis*-β-chlorovinylmercury chloride. A singlet at 33.132 MHz was observed in the ^{35}Cl NQR spectrum, its position apparently indicating the absence of intermolecular coordination, as happens in the *trans*-isomer[219]. Whereas the dipole moment of the *trans*-isomer agrees well with the calculation, for the *cis*-isomer there is a sharp discrepancy between the observed and calculated moments in benzene (2.92 and 3.57 D respectively), which is believed[220] to be caused solely by the appreciable decrease of the ClCC and CCHg angles in consequence of the intramolecular coordination. Using different solvents (benzene, dioxan, and ethyl acetate), it has been shown by the same method that the strength of the Cl → Hg intramolecular coordinate bond in *cis*-ClCH = CHHgHal decreases in the sequence Cl > Br > I,[221] while strong intermolecular Hal → Hg bonds have been observed in the corresponding *trans*-analogues (on the basis of Hal NQR spectra)[222]. Intramolecular coordination probably occurs also in di(*cis*-β-chlorovinyl)mercury, since $J_{^{13}C-^{199}Hg}$ in the ^{13}C NMR spectrum is appreciably higher than for symmetrical mercury compounds, where coordination is known to be ruled out[223].

Finally, the *cis*-β-chlorovinylmercury chloride molecule has been investigated by gas electron diffraction (R = 11.5%)[224]. The intramolecular non-valent Hg...Cl distance proved to be 3.27 Å, while the sum of the van der Waals radii is 3.3–3.5 Å. Consequently the electron-diffraction data are consistent with the occurrence of extremely weak intramolecular coordination, but cannot be regarded as unambiguous proof. The decrease of the CHgCl angle, located opposite the additional chlorine atom, to 168.5° might also indicate intramolecular coordination, but it is not clear in which direction the Hg–Cl bond is "bent". Presumably the intramolecular coordination is largely determined by the rigidity of the molecular geometry:



Nevertheless the mercury atom in the *cis*-isomer is coordination-saturated and the *cis*-chloride does not therefore form complexes with pyridine[225], TMEDA, and di(mercaptomethyl)ethane[226], in contrast to the *trans*-chloride. For this reason, nucleophilic attack on the mercury atom should be hindered in the *cis*-isomer, which in turn hinders the nucleophilic cooperation in electrophilic substitution at the carbon atom.

Apart from considerable resistance to electrophilic substitution, *cis*-β-chlorovinylmercury chloride does not eliminate acetylene even when acted upon by powerful nucleophilic agents, i.e. lacks completely the capacity to transfer the reaction centre and therefore lacks "dual" reactivity. For example, whereas the *trans*-isomer immediately evolves acetylene even when acted upon by a weak nucleophilic agent such as dibutylmercury, the *cis*-isomer is readily alkylated by Grignard reagents[226-228]:

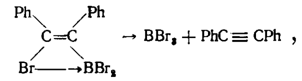


R=Me, Ph, etc.

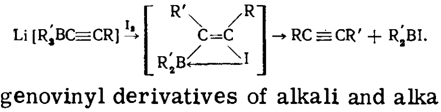
It has been shown that the *cis*-compound is also smoothly symmetrised on treatment with iodide ions, in contrast to the *trans*-compound, which immediately evolves acetylene[227,228]. Both stereoisomers react with diazomethane without the evolution of acetylene and with formation of the corresponding β-chlorovinyl(chloromethyl)mercury compound, which then eliminates acetylene under thermodynamically-controlled conditions[226-228].

The study of the thermolysis of β-chlorovinyl derivatives of mercury has shown[229] that the stability of *cis*-ClCH-CHHgHal decreases in the sequence Cl > Br > I, while the inverse series holds for the *trans*-isomers. However, this behaviour in the case of the *cis*-compounds is inconsistent with the decrease of the strength of intramolecular coordination in the sequence observed in the measurement of dipole moments[221]. The mass spectra of the *cis*- and *trans*-compounds are qualitatively the same, but the *cis*-isomers are more stable under electron impact.

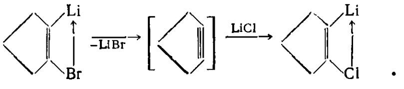
Unfortunately the strength of intramolecular coordination has not been investigated for different halogens in the halogenovinyl group, since such compounds could not be synthesised despite numerous attempts. Nevertheless the strength of intramolecular coordination should presumably increase in the sequence Cl < Br < I, by analogy with boron derivatives. The series is fairly clear for the latter. Indeed *cis*-β-chlorovinylboron distills *in vacuo* without decomposition and is smoothly arylated by di-(*p*-anisyl)mercury to *cis*-β-chlorovinyl(dianisyl)boron.[226] β-Bromovinyl compounds decompose to acetylenes on slow heating *in vacuo*[230]:



while β-iodovinyl compounds cannot be isolated at all because they are converted quantitatively into acetylenes even under mild conditions (–78°C)[231]:

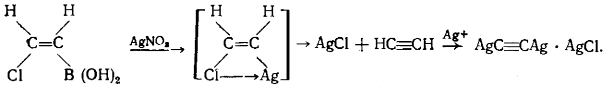


β-Halogenovinyl derivatives of alkali and alkaline earth metals are still less stable. Thus 2-bromo-1-lithiocyclopentane eliminates a very unstable monomolecular cyclopentyne at a temperature as low as 20°C (this has been established on the basis of the concentration variation of the salt effects and the reversibility of the formation of lithium bromide) via a first-order reaction with an activation energy of 24 kcal mole⁻¹ (± 10%). In its thermolysis in the presence of 2,5-diphenyl-3,4-benzofuran, the product of addition to cyclopentyne, the formation of which in the course of the reaction had been demonstrated kinetically, was isolated. Lithium chloride adds to cyclopentyne with formation of 2-chloro-1-lithiocyclopentene:[232]

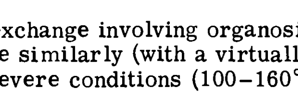


Cyclohexyne and cycloheptyne have been obtained under mild conditions from 2-fluoro-1-lithiocyclohexene and a Grignard reagent, based on 1,2-dibromocycloheptene, respectively[233,234]. Their formation has been demonstrated by condensation and trimerisation reactions and is undoubtedly due to M ← Hal intramolecular coordination (M = Li or MgHal).

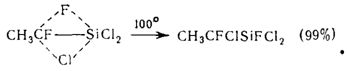
β-Chlorovinyl derivatives of silver are also extremely unstable. When an attempt was made to obtain them by treating stereochemically pure *cis*- and *trans*-β-chlorovinylboronic acids with aqueous silver nitrate solution, only the complex of silver carbide with silver chloride AgC≡CAg.AgCl was isolated. The initial state probably involves the formation of *cis*- and *trans*-β-chlorovinyl derivatives of silver, which eliminate acetylene as a result of Ag ← Cl intramolecular or intermolecular coordination, and the acetylene is metallated by the excess silver ions[235]:



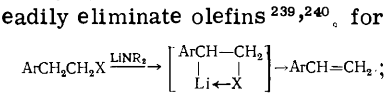
When the chemical consequences of intramolecular coordination in aliphatic systems are considered, one must remember the spontaneous diatropic intramolecular rearrangement of α-halogeno-organoboranes with hydride substitution of halogen and the formation of alkylhalogenoboranes, which proceeds via a first-order reaction with inversion of configuration[236,237]:



An analogous exchange involving organosilicon compounds takes place similarly (with a virtually quantitative yield) but under severe conditions (100–160°C) when there are different halogens at the silicon and α-carbon atoms, for example[238] (see also Brook and Jones[161]):



β-Halogeno-derivatives of alkali metals are extremely unstable and readily eliminate olefins[239,240], for example:

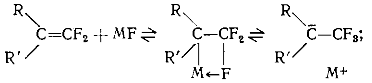


$$\mathrm{ArCH_2CH_2X}\xrightarrow{\mathrm{LiNR_2}}\left[\begin{matrix}\mathrm{ArCH{-}CH_2}\\ |\qquad |\\ \mathrm{Li\leftarrow X}\end{matrix}\right]\rightarrow\mathrm{ArCH{=}CH_2};$$

X=Cl, Br, OSO_2, Ph.

These compounds can be obtained at very low temperatures with a yield not exceeding several per cent[174].

In the case of organofluorine compounds β-elimination may be in equilibrium with the reaction involving the addition of the metal fluoride to the olefin:

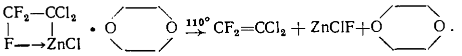


M = metal .

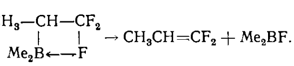
The position of such equilibrium depends on many factors, but probably mainly on the M–F bond energy. In fact LiF and NaF, which hardly add to fluoro-olefins, have a much higher M–F bond energy than KF and CsF, which readily form carbanions on interaction with perfluoro-isobutene and perfluoropropene.

Aliphatic Grignard reagents can be obtained only when there is no heteroatom other than fluorine in the β-position (see Section I and also Ballard and Gilman[241]).

Organozinc compounds possess the same properties[242,243]; one should note that β-elimination takes place much more readily than α-elimination even in the case of relatively unreactive halogens[243]:

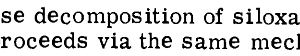


β-Halogenoboron compounds are extremely unstable and usually decompose already at the instant of formation[244-249]. Even the most stable of the compounds described remain stable only at −78°C and begins to decompose slowly at room temperature and rapidly at 100°C [246]:



$$\begin{matrix}\mathrm{CH_3{-}CH{-}CF_2}\\ |\qquad\ |\\ \mathrm{Me_2B\longleftarrow F}\end{matrix}\rightarrow\mathrm{CH_3CH{=}CF_2+Me_2BF}.$$

β-Fluoroethylsilanes eliminate ethylene in the gas phase only at 150–320°C via a first-order reaction. The rate of reaction is independent of the surface to volume ratio of the reaction vessel, pressure, and the presence of radical traps—cyclohexene and nitric oxide[250-254]:

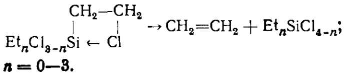


$$\begin{matrix}\mathrm{CH_2{-}CHF}\\ |\qquad |\\ \mathrm{X_3Si\longleftarrow F}\end{matrix}\rightarrow\mathrm{X_3SiF+CH_2{=}CHF};$$

X=F, OMe, OBu, Me.

The liquid-phase decomposition of siloxane with X = OBu in a silicone oil proceeds via the same mechanism[255]. β-Fluoroethylpolysiloxanes of the type $[CHF_2CH_2SiO_{1.5}]_n$ behave similarly[255-256].

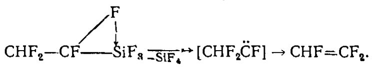
β-Chloroethylsilanes decompose in the gas phase at 300–400°C also via a first-order reaction, the rate of reaction increasing on replacement of alkyl substituents at the silicon atom by chlorine[257-260]:



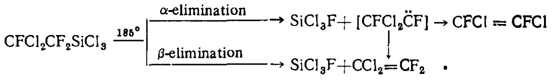
$$\begin{matrix}\mathrm{CH_2{-}CH_2}\\ |\qquad |\\ \mathrm{Et_nCl_{3-n}Si\leftarrow Cl}\end{matrix}\rightarrow\mathrm{CH_2{=}CH_2+Et_nSiCl_{4-n}};$$

$n = 0$–3.

When fluorine atoms are present simultaneously in the α- and β-positions with respect to silicon, α-elimination takes place exclusively[251,261-263], for example;

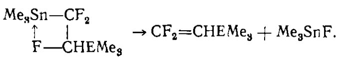


On the other hand, when different halogens are present in the α- and β-positions in the molecule, α-elimination clearly predominates over the possible β-elimination or the 1,2-shift of the fluorine atom in the carbene formed (the yields of olefins are 80 and 7% respectively)[263,264]:



It is difficult to account for this mode of thermolysis. Purely conformational factors probably play a decisive role here.

Mixed polyfluoroethyl derivatives of the type $Me_3SnCF_2CFHEMe_3$ (E = Si, Ge, or Sn) decompose at much lower temperatures (55°C, 20°C, and at the instant of preparation) and exclusively via β-elimination[265,266]:



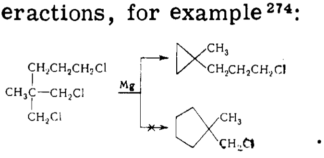
$$\begin{matrix}\mathrm{Me_3Sn{-}CF_2}\\ \uparrow\qquad |\\ \mathrm{F{-}CHEMe_3}\end{matrix}\rightarrow\mathrm{CF_2{=}CHEMe_3+Me_3SnF}.$$

These findings can be accounted for both by a decrease of the E–C bond energy in the sequence Si > Ge > Sn and by the sharp increase of the coordinating capacity of E in the reverse sequence. Conformational factors probably also play a significant role, since $l_{\mathrm{Sn-F}_\alpha} > l_{\mathrm{Sn-F}_\beta}$.

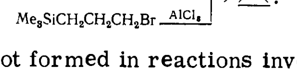
Compounds of the type $Me_3ECF_2CHFM(CO)_5$ (where E = Ge or Sn and M = Mn or Re) also decompose similarly at the instant of formation[267-269].

If the fluorine atom is in the γ-position, then organic derivatives of the elements (for example, derivatives of magnesium[270], boron[270], and silicon[271]) acquire enhanced stability and decompose via a radical-chain mechanism[271]. The lack of coordinating capacity by the fluorine atom in the γ-position has not been satisfactorily explained.

On the other hand, other halogens in the γ-position decrease sharply the stability of organometallic compounds and it is actually impossible to isolate them in the case of reactive metals. For example, magnesium[272-275], zinc[276], and aluminium[245] compounds readily eliminate substituted cyclopropanes. The tendency towards intramolecular 1,3-interaction is very great and clearly predominates over 1,4- and 1,5-interactions, for example[274]:

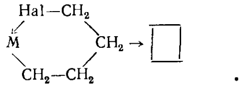


It is interesting that γ-halogenopropyl derivatives of boron[244] and silicon[277] are thermally stable. Nevertheless cyclopropane is readily formed from the silicon compounds[277] either as a result of a base-catalysed elimination (in which the carbanion formed in the ionisation of the Si–C bond undergoes intramolecular nucleophilic substitution) or under the influence of aluminium chloride, which involves the intramolecular electrophilic substitution of the carbonium ion formed on ionisation of the C–Hal bond:



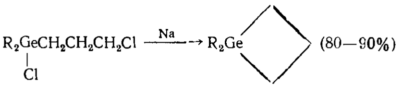
Cyclopropane is not formed in reactions involving the exchange of the reactants.

δ-Halogenobutyl derivatives of reactive metals (sodium, lithium, magnesium[278], and aluminium[196]) decompose only at elevated temperatures with slight (11–13%) elimination of cyclobutane (CB):

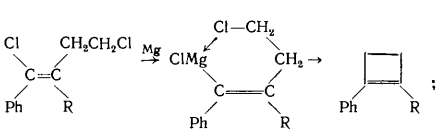


However, similar aluminium compounds have been found[245] to give rise on decomposition exclusively to methylcyclopropane and but-1-ene, but not cyclobutane.

An exception to this rule is the cyclisation of γ-halogenopropyl-silanes and -germanes[279,280] under the influence of sodium in boiling toluene, for example:

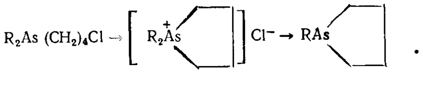


and of an unusual Grignard reagent formed from 1,4-dichlorobut-1-enes in ether (the yield of cyclobutene reaches 90%) where magnesium reacts with the vinyl chlorine and not the primary chlorine[281]:

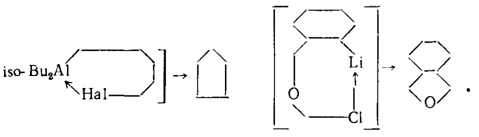


R=H, Ph.

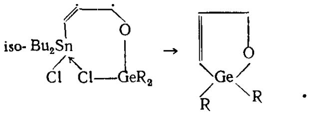
δ-Cyclobutyl derivatives of arsenic form five-membered rings at 160–170°C in 80% yield[282,283], while compounds with longer or shorter aliphatic chains are thermally stable:



Cyclisation reactions of ε-halogeno-derivatives of lithium[284], and aluminium[196] have also been described; these have not been isolated, but a Hal → M linkage has been postulated on the basis of the high yields of reaction products (70 and 75% respectively):



The reactions of γ-siloxy(germyloxy)chlorostannanes at temperatures exceeding 130°C with formation of oxametallocyclo-alkanes and -alkenes[285] have also been described, for example:

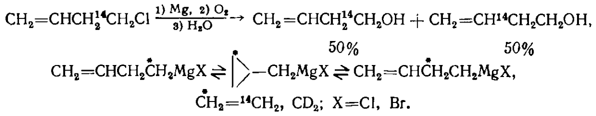


V. COMPLEXES WITH π-LIGANDS

In contrast to transition metals, which readily form stable π-complexes playing an extremely important role in modern chemistry, particularly in the stereochemically controlled reactions of π-electron systems, such complexes of non-transition metals have been obtained only recently for bivalent germanium, tin, and lead (see, for example, the paper by Doe et al.[286] and the references quoted there). At the same time, it has been shown in numerous investigations that, although many ω-unsaturated organometallic compounds derived from Group IA–IIIA metals cannot in fact be isolated in a pure state, they are undoubtedly formed as intermediates in solutions and cyclise very rapidly as a result of M ← π-ligand intramolecular coordination.

1. Olefins

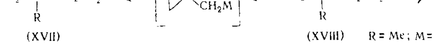
This new branch of the chemistry of organometallic compounds was begun by a study[287] in which the Grignard reagent obtained from the deuterium-labelled or [^{14}C] allylmethyl chlorde (bromide) was oxidised by oxygen in ethereal solution. The distribution of the label along the chain in the unsaturated alcohols obtained demonstrated unambiguously that the Grignard reagent cyclises before its oxidation to the alcohol:



The ^1H NMR spectra show that ⩾ 99% of the Grignard reagent from arylmethyl chloride (bromide) and from cyclopropylmethyl chloride has the allylmethyl structure. This had been established by the author in an earlier study[288]. The time of 50% equilibration between the isomeric acyclic forms of the Grignard reagent is 30 h at 27°C and 40 h at 55°C and corresponds to an activation energy of 23 kcal mole^{-1}.

The existence of the cyclic form has been demonstrated by the fact that treatment of cyclopropylmethyl bromide (chloride) with magnesium in methyl ether (–24°C) or in ethyl ether (36°C) in the presence of traces of benzoic acid yielded methylcyclopropane, the content of which reached 55% in the case of the bromide[289]. This amount should correspond to the initial cyclic form, whose protonation is much faster than its rearrangement. The rearrangement proceeds via a first-order reaction and its 50% reaction time is about 2 h at –24°C, which corresponds to a free energy of activation of 19 kcal mole^{-1}.

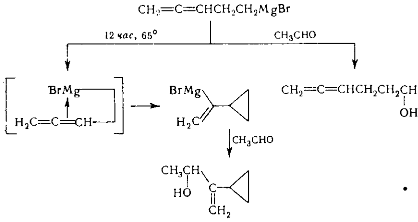
The study of the influence of substituents in the γ- and δ-positions on the rearrangement of allylmethyl Grignard reagents showed that the vinyl group or two phenyl groups in the δ-position appreciably accelerate the rearrangement in consequence of the stabilisation of the partial negative charge in the cyclic forms. Thus, when phenyl groups are present, the distribution of the deuterium label between the α- and β-positions was completed in 5 h at room temperature, the content of the cyclic form being less than 0.3%.[290] Conversely, the phenyl group in the γ-position appreciably retards the formation of the cyclic form, probably in consequence of the destabilisation of the cyclopropane ring. According to ^1H NMR spectra, compound (XVII) is stable in ethers at room temperature and rearranges to (XVIII) only after 8 h at 100°C.[291] The study of the reversible isomerisation (XVII) ⇌ (XVIII), i.e.



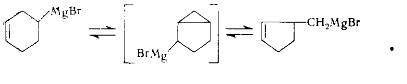
(XVII) (XVIII) R = Me; M = Li, MgBr.

by ^{1}H NMR [292] showed that the rate of equilibration depends on the following factors: (1) the structure of the organic group; (2) temperature; (3) the electronegativity of the metal (it decreases in the sequence Li $\gg R_2Mg > RMgX$); (4) the solvent (in more polar solvents, the isomerisation is retarded for magnesium compounds but accelerated for lithium compounds); (5) the concentration (it increases linearly for Grignard reagents, the proportionality constant depending particularly strongly on the temperature, solvent, and substituents; on the other hand, for the lithium compound it depends appreciably on the concentration); (6) the presence of salts in solution [$MgBr_2$ accelerates the rearrangement of (XVII), while lithium alkoxides retard it]. Furthermore, compounds (XVIII) predominate in the equilibrium mixture in consequence of the very pronounced thermodynamic secondary isotope effect and the (XVII) $\rightleftharpoons$ (XVIII) equilibrium constant depends on the physical conditions. The authors explain [292] the results by the existence of two different mechanisms of the reversible isomerisation (XVII) $\rightleftharpoons$ (XVIII): an ionisation-recombination process for lithium compounds and a bimolecular process for organomagnesium compounds, probably via an *at* complex.

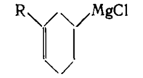
The allene system apparently constitutes the limiting case of the stabilisation of the cyclic form (because of the absence of decyclisation) and it is therefore of preparative importance for the synthesis of vinylcyclopropanes. For example, the yields of the Grignard reagent from 5-bromopenta-1,2-diene in THF and of the cyclic and straight-chain alcohols derived from it (respectively after refluxing for 12 h and without heating, with subsequent treatment with acetaldehyde) proved to be 25%, which indicates a quantitative cyclisation reaction with a 50% decomposition period of about 4 days at 25°C [293]:



The rearrangements of cyclic allylmethyl Grignard reagents have also been investigated. While the cyclopentene compound decomposes on heating without change in ring size, the cyclohexene and methylcyclopentene Grignard reagents undergo interconversions, the latter greatly predominating in the equilibrium mixture (about 90% after several hours at 80°C) [294-296]:



It has been shown with the aid of deuterium labels that the rearrangement proceeds via a bicyclic intermediate, which, however, cannot be determined in the equilibrium mixture. The authors believe that the driving force of the ring contraction process [294-296] is the difference between the stabilities of the primary and secondary Grignard reagent, which they estimated as 3.7 kcal mole^{-1}. The equilibrium constant depends strongly on the solvent and concentration, and a secondary entropy-controlled isotope effect is observed for the deuterated compounds:



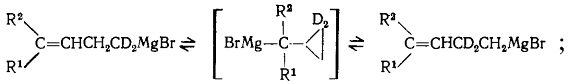
;

R=H, Ph, p-MeC_6H_4, m-$CF_3C_6H_4$.

(XIX)

Comparison of the rates of rearrangement to compound (XIX) showed that an aryl group decreases and electronegative substituents slightly increase the rate. These results correspond best to isomerisation with ClMg ← ‖ intramolecular coordination via a bicyclic intermediate, which is formed at a lower rate than that of its decomposition to the cyclopentene ring [297]. Furthermore, the signals of the olefinic protons in the ^{1}H NMR spectra of the initial Grignard reagents are located in a lower field compared with the corresponding hydrocarbons, which the authors [297] believe may serve as evidence for the formation of π-complexes.

This mechanism was confirmed in a study of the kinetics of the reversible isomerisation (XX) $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ (XXII), i.e.

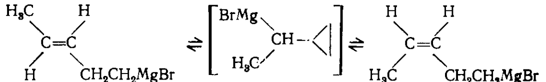


(XX) (XXI)

(a) R^1=H, R^2=Me; (b) R^1=R^2=Me ,

(XXII)

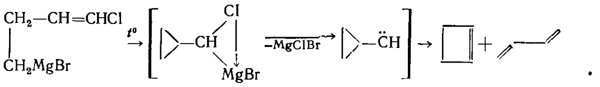
by ^{1}H NMR in ether [298]. It was found that compound (XXa) (*cis* : *trans* = 42 : 58) is in equilibrium with compound (XXII) only after 775 h at 100°C. The rearrangement is retarded even more after the introduction of a second methyl group in the δ-position: compound (XXb) gives rise to (XXIIb) after 900 h at this temperature with a yield of only 20%. These results conflict with a radical mechanism. To demonstrate the involvement of the intermediate (XXI), which cannot be detected in the equilibrium mixture, a study was made of the kinetics of the *cis*-*trans* isomerisation (XXIII) $\rightleftharpoons$ (XXV) with gas-liquid chromatographic identification of the carboxylated reaction products in the form of their methyl esters. Regardless of the initial compound, (XIII) or (XXV), the isomerisation was described by a first-order equation and always led to the same mixture of *cis*- and *trans*-products (21 : 79). Since the sums $k_1 + k_2$ for the equilibria (XXa) (XXIIa) and (XXIII) (XXV) are of the same order of magnitude, (XXI) and (XXIV) are true intermediates, in which the single bond between the carbanionic centre and the cyclopropane ring has sufficient time for free rotation. The *cis*-*trans* isomerisation (XXIII) $\overset{k_1}{\rightleftharpoons}$ (XXV) therefore proceeds via the same mechanism as the reversible isomerisation involving the α- and β-positions in the (XX) $\rightleftharpoons$ (XXII) process [298]:



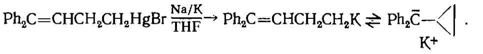
(XXIII) (XXIV) (XXV) .

When a chlorine atom is introduced into the δ-position, the Cl → Mg intramolecular coordination occurs with formation of cyclopropylcarbene, since thermolysis of the Grignard reagent in ethers yielded cyclobutene in 80% yield together with a small amount of buta-1,3-diene (detected by ^{1}H NMR) [299]. The 50% decomposition period of the initial compound in THF is 500 h at 61.5°C and 2 h at

107°C, which corresponds to an activation energy of 30 kcal mole^{-1}:

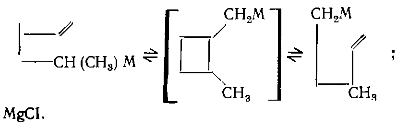


The dependence of the cyclisation–decyclisation reaction on the amount of ionic character of the metal–carbon bond has been investigated[300]. When the allylmethyl compound of mercury is added to the sodium–potassium alloy in THF, a dark cherry-red solution of the cyclic anion is formed immediately, giving rise after carboxylation to phenylcyclopropylacetic acid in 80% yield. The replacement of potassium by sodium also leads to the cyclic product only:



Its stability is explained by the stabilisation of the electron pair by the benzene rings. On the other hand, when the potassium in ether is replaced by lithium or magnesium, which form stronger covalent bonds with carbon, there is an immediate reverse rearrangement to the corresponding acyclic products. These rearrangements are reversible. For example, diphenylcyclopropylmethyl-lithium is stable in THF, while in ether it isomerises completely to $\gamma\gamma$-diphenylallylmethyl-lithium. The reverse rearrangement can be induced by the simple addition of THF to an ethereal solution the compound.

In systems containing a four-membered ring there is also equilibrium between the acyclic and cyclic forms of the organometallic compounds, for example[301]:



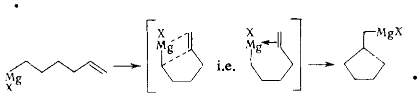
M=Li, MgCl.

In THF, the Grignard reagent rearranges much more slowly than the sodium and lithium compounds, despite the use of less polar hydrocarbons as solvents for the latter. The equilibrium mixture obtained for the organolithium derivative contains more than 99% of the primary compound, which indicates its higher stability compared with the isomeric secondary compounds. It is believed that this isomerisation proceeds via a four-membered cyclic intermediate.

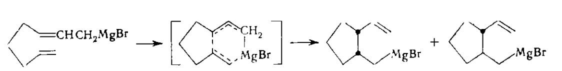
Equilibrium is established in such systems at a very high rate. For example, it is 3×10^{-6} s^{-1} at 140°C and 3.5×10^{-5} s^{-1} at 160°C (obtained from the rate of appearance of α-protons in the ^{1}H NMR spectrum) for deuterated organomagnesium compounds, the isomer concentrations at equilibrium being in proportions of 3 : 2.[302]

It is important to note that cyclobutane does not form even in trace amounts in the isomerisation of allylmethyl compounds[290,291].

Because of the low angular ring strain, cyclopentyl derivatives of metals are fairly stable, but their stability depends strongly on the nature of the organic group. Thus the primary Grignard reagent obtained from 7-bromohept-1-ene forms 7% of methylcyclohexane [303], while the secondary Grignard reagent (from 6-chlorohept-1-ene) gives after hydrolysis a mixture of *cis*- and *trans*-1,2-dimethylcyclopentanes in proportions of 1 : 4 with a yield of 88% [304]:

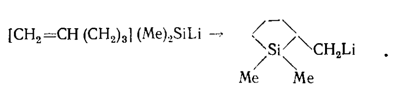


The secondary Grignard cyclises faster than the primary or tertiary reagent in THF at 100°C, all the rearrangements proceeding via first-order reactions. The observed ratios of the *cis*- and *trans*-products undoubtedly indicate an intramolecular mechanism of these reactions (an intermolecular interaction of a Grignard reagent with an isolated double bond is unknown with the exception of the addition of ethylene to allylmagnesium chloride)[305]:

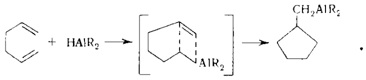


The isomerisation is highly stereoselective. Thus, when an ethereal solution of diene was refluxed, it cyclised smoothly with formation of *cis*- and *trans*-products in yields of 90 and 3% respectively and a 50% decomposition period of 2 h.[306]

Cyclisation involving the formation of cyclopentanes also occurs in the series of organolithium compounds, for example with $CH_2 = CH(CH_2)_3CHRLi$ (R = H or Me) [307], norbornene systems[308], and silicon-lithium derivatives[309], the process being quantitative in the last instance:

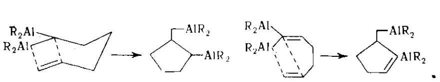


Organic derivatives of Group III metals, particularly aluminium compounds, play an important role in the formation of cyclopentanes. Using these, Ziegler[310] achieved for the first time the cyclisation reaction in the chemistry of ω-unsaturated organometallic compounds. He showed that the interaction of dialkylaluminium hydride with hexa 1,5-dienes gives a quantitative yield of α-aluminomethylcyclopentanes:



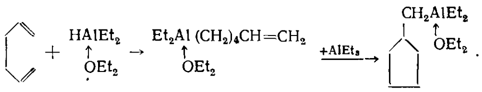
Subsequently this reaction was extended to strained 1,5-dienes[311].

The mode of hydroalumination of vinylacetylenes with subsequent cyclisation can be controlled by choosing an appropriate solvent. For example, the reaction involving hex-1-en-5-yne in ether with subsequent hydrolysis gave the cyclopentane derivative an 80% yield, while in triethylamine the reaction leads to cyclopentenes with the same yield[312]:



The reaction of trialkylaluminium with buta-1,3-dienes also leads to cyclopentanes (yield 27%).[313]

All the reactions described above proved to be feasible only because the cyclisation is faster, even at low temperatures, than the intramolecular addition of dialkylaluminium hydrides to the terminal double bonds. However, such cyclisation can be prevented with the aid of specific coordination. For example, it does not occur with the $Et_2AlH \leftarrow OEt_2$ ether adduct, the acyclic product being formed in 93% yield ($>$Al ← ‖ intramolecular coordination is impossible), but the adduct can cyclise quantitatively following the addition of a catalytic amount of triethylaluminium, which decomposes the complex and liberates the ω-unsaturated organoaluminium compound[314]:



A general method has been proposed for the cyclisation of hex-5-enyl organometallic compounds based on the exchange reaction between dihex-5-enylmercury and the corresponding metal[315]:

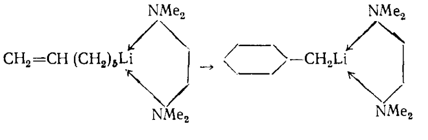
$$\frac{n}{2}\,\mathrm{Hg}\,[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_2 + mM \rightarrow mM\,[(\mathrm{CH_2})_4\mathrm{CH{=}CH_2}]_n \rightarrow$$
$$\rightarrow mM\,[\mathrm{CH_2}\,(\text{cyclo- }\mathrm{C_5H_{12}})]_n;$$
$$M{=}\mathrm{Li,\ Mg,\ Al,\ Ga,\ In.}$$

In non-coordinating solvents, the formation of a ring requires between 1 h and 8 days at 25°C for M = Li (depending on the solvent; 1 h in ether), 24 h at 110°C for M = Mg, 48 h at 40°C for M = Al, 3 weeks at 95°C for M = Ga, and 3 weeks at 110°C for M = In (the reaction times were determined from ^{1}H NMR spectra). The solvent plays a major role in determining the rate of exchange and cyclisation[316]. For lithium, the rate increases in the sequence cyclopentane $<$ benzene $\ll$ ethyl ether (8 days, 96 h, and 1 h respectively); the aluminium compound could not be isolated from hydrocarbons, while in THF the reaction does not proceed at all and in ethyl and phenyl ethers it occurs to the extent of 4.9 and 95% respectively. These results are consistent with the known behaviour of organolithium compounds in basic media, where intermolecular linkages are broken, which leads to an increase of their reactivity. The opposite effect is observed for aluminium compounds.

It is remarkable that these rearrangements proceed much more readily than the analogous intermolecular reactions. However, they do not occur with but-3-enyl and pent-4-enyl derivatives of metals because of the high strain in the three- and four-membered rings[315].

The ease of cyclisation of hexenyl derivatives of metals decreases in the sequence Al $>$ Mg $>$ Li $>$ Zn $\gg$ Hg[317] (for zinc, the cyclisation takes place to a very slight extent). This sequence is probably determined by the presence of vacant orbitals in the metal and the polarity of the M–C bond.

On the other hand, the heptenyl derivatives of lithium and magnesium do not form six-membered rings either in ether or in THF, but in the presence of TMEDA, which greatly increases the polarity of the M–C bond, they cyclise readily and irreversibly (special experiments showed that the cyclopentylmethyl and cyclohexylmethyl derivatives of lithium and magnesium are not decyclised in the presence of TMEDA)[307]:



Similar aluminium compounds form cyclohexanes at an elevated temperature[318] in yields up to 70%[316], while octenyl derivatives of aluminium do not cyclise to cycloheptanes.[316]

The comparatively ready cyclisation of ω-unsaturated organometallic compounds should be preceded in many instances by M $\leftarrow \|$ intramolecular coordination in non-reacting molecules, which has been studied in a number of investigations using various physicochemical methods.

Weak Li $\leftarrow \|$ intramolecular coordination has been postulated in but-3-enyl-lithium[319] on the basis of ^{7}Li and ^{1}H NMR and infrared and ultraviolet spectroscopic data, which indicate anomalous properties of the double bond.

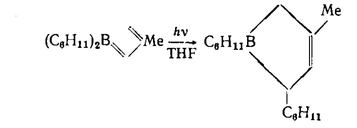
The chain length in olefins has little influence on the electronic environment of the double bond, but the introduction of groups in the terminal positions alters the chemical shifts of the olefinic protons, which are in general correlated with the electron-donating or electron-accepting properties of the substituents. For example, dibut-3-enyl- and dihex-5-enyl-zinc have the normal parameters of the ^{1}H NMR spectrum (the signals of the olefinic protons are located in the same region as for the corresponding pure alkenes) and there is no coordination interaction in these compounds. On the other hand, the spectrum of dipent-4-enylzinc is anomalous: compared with pent-1-ene, the chemical shifts due to the protons of the olefinic and α-carbon atoms are displaced downfield owing to the decreased electron density at the double bond. Furthermore, the signals due to the α-protons are displaced downfield even more at –70°C or on formation of a complex with 2,2′-bipyridyl. These data suggested the existence of weak Zn $\leftarrow \|$ intramolecular coordination[317,320]. It was impossible to study dipent-4-enylmagnesium by a similar procedure because of its insolubility in coordinating solvents, and in the analogous mercury compound there is no such coordination[320].

Alkenyl derivatives of Group III metals exhibit the same characteristics. For example, in the infrared spectra of alk-4-enyl derivatives of aluminium the band due to the ν(CH) deformation vibrations of the olefinic linkage is displaced by 30–38 cm^{-1} towards shorter wavelengths and the band due to the ν(C=C) vibrations is displaced by 22–23 cm^{-1} towards longer wavelengths compared with the initial olefins. The compounds are monomeric in benzene and their spectra change following dilution by hydrocarbons. However, the $\geqslant$Al $\leftarrow \|$ intramolecular coordinate linkage is ruptured under the influence of Lewis acids, since ether adducts, for example, have the normal ν(CH) and ν(C=C) frequencies. Intramolecular coordination in non-reacting alk-4-enylaluminium compounds (cyclisation occurs only at elevated temperatures) is confirmed additionally by ^{1}H NMR spectra where the $\delta_{\mathrm{CH=CH}}$ signals are displaced downfield by 0.3 p.p.m., while the $\delta_{\mathrm{CH_2}}$ signals of the isobutyl groups are displaced upfield by 0.15 p.p.m., compared with the 6- and 7-enyl homologues of aluminium, in which there is no coordination (no frequency shifts were observed in the spectra)[321].

It is interesting to note that the signals of the olefinic protons are displaced upfield also on formation of a complex with trimethylamine, and the shifts are independent of concentration. This clearly indicates an intramolecular mechanism of these processes. The energy of the $\geqslant$Al $\leftarrow \|$ intramolecular coordinate bond has been estimated as at least 2–5 kcal mole^{-1}.[322]

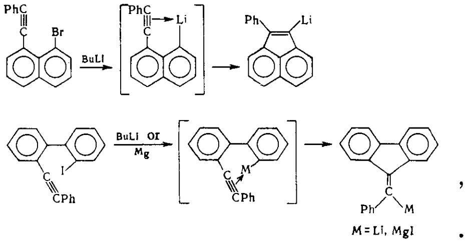
^{1}H, ^{13}C, and ^{119}Sn NMR and infrared and Mössbauer spectra have shown[323,324] that there is no M $\leftarrow \|$ coordination in the alkenyl derivatives of Group IV elements of type $\geqslant\mathrm{M(CH_2)}_n\mathrm{CH = CHR}$ (M = Si, Ge, or Sn; n = 1 or 2; R = H or Ph).

The photochemical cyclisation of dienylboranes to boracyclopent-3-ene is exceptional [ν(C=C) = 1635 cm^{-1}; monomeric state in benzene[325]] and probably proceeds via intramolecular coordination:

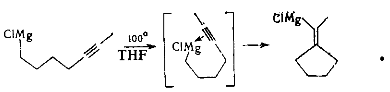


2. Acetylenes

The intramolecular addition of organometallic compounds to an isolated acetylenic bond has been little investigated, but is of considerable practical interest for the synthesis of various classes of vinyl compounds. It has been shown that such interaction in rigidly fixed systems depends on the relative positions of the C≡C triple bond and the M–C bond.[326,327] For example, when 8-bromo-1-phenylethynylnaphthalene is metallated with butyl-lithium, it cyclises, but the cyclisation reaction does not proceed with the corresponding Grignard reagent. The difference is undoubtedly associated with the much higher polarity of the C–Li bond compared with C–Mg. The carbon skeleton of 2-chloro-1-phenylethynylbenzene does not change when chlorine is replaced by lithium or magnesium, while treatment of 2-iodo-2′-phenylethynylbiphenyl with butyl-lithium or magnesium results in cyclisation to a five-membered ring:

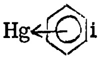


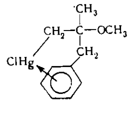
Aliphatic systems with triple bonds may be of preparative importance for the synthesis of ethylidenecyclopentanes. For example, when the Grignard reagent derived from 7-chlorohept-2-yne is refluxed for 6 days at 100°C with subsequent hydrolysis, the yield is 90%; however, the yield falls to several per cent in the absence of refluxing. There is no doubt that the isomerisation takes place after the formation of the Grignard reagent, the 50% cyclisation period of which is 50 h at 100°C:[328]

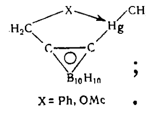


Similar reactions with 7-halogeno-oct-2-ynes yield substituted ethylidenecyclopentanes, the 50% cyclisation period for the bromide, amounting to about 15 h at 100°C. Like the alkenyl derivatives, secondary alkynyl Grignard reagents cyclise faster than the primary reagents, the smaller of the two possible rings being formed, i.e. ethylidenecyclopentanes and not the more stable methylcyclohexenes.[305,328]

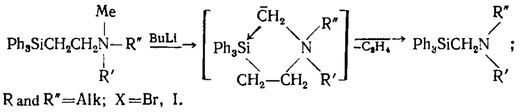
3. Aromatic Compounds and Carbanions

According to ^1H NMR spectra, Hgintramolecular coordination probably occurs in 2-methoxy-2-methyl-3-phenylpropylmercury, since the methylene protons are found to be non-equivalent, the non-equivalence diminishing sharply when strong solvating solvents, for example pyridine, capable of breaking the coordinate linkage, are used[329]. J_{HgCCCH_3} changes in the same way. A similar interaction has also been proposed for methylmercury derivatives of carboranes in view of the similar influence of solvents on $J_{^{199}Hg-C-^{1}H}$.[330]





A very rare instance of possible intramolecular coordination with a carbanion has been described recently. Three base-catalysed rearrangements of quaternary ammonium salts are known—the Stevens, Sommelet-Hauser, and Hofmann rearrangements. On the other hand, a specific rearrangement of the molecular skeleton of silicon derivatives takes place. When silylethylammonium salts were treated with an excess of butyl-lithium and then with water, silylmethylamines were obtained as the main product[331] and the Stevens rearrangement was not observed:



The amines are probably formed as a result of intramolecular attack by the negative charge on the silicon atom in the intermediate carbanion, which leads to the ejection of ethylene. In the case of R″ = Ph, there is no rearrangement and only *NN*-dimethylaniline has been isolated.

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The data described demonstrate convincingly the increasing importance of intramolecular coordination for the understanding of many aspects of the structure and reactivity of organic derivatives of the elements, and particularly its decisive involvement in preparative syntheses of many classes of organic compounds, the preparation of which by other methods is either difficult or impossible. On the other hand, the concept of intramolecular coordination has not been justified theoretically and it is often difficult to demonstrate it experimentally. However, this field of the chemistry of organic derivatives of the elements began to develop vigorously only recently and holds out much promise for the immediate future.

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Advances in the Synthesis of Heteroadamantanes

N.V.Averina and N.S.Zefirov

Typical formal schemes for the synthesis of heteroadamantane structures and the limits of applicability and synthetic scope of various methods are discussed and described systematically.
The bibliography includes 207 references.

CONTENTS

I. INTRODUCTION

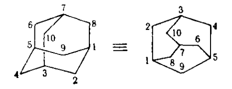
More than 1000 publications have been devoted to the synthesis and study of the properties of adamantane and its derivatives and their number has been continuously increasing. Such persistent interest by chemists is due to a set of unique properties of compounds of the adamantane series, which makes this class interesting from both theoretical and practical points of view. A large number of reviews have been devoted to the chemistry of adamantane, some of which are concerned only with synthetic aspects[1-4], while others deal more or less completely with the entire set of problems in the chemistry of adamantanes and their practical applications[5,6]. Heteroanalogues of adamantane constitute an important class of compounds. There are two reviews on heteroadamantanes covering the literature up to 1961, but these are to a large extent obsolete[1,4]. Although other reviews[7,8] were published later (partly covering the literature up to 1967), they are insufficiently complete. There has been recently a considerable growth of the number of publications dealing with the synthesis of heteroadamantanes and the search for novel methods of synthesising them and with the study of the chemical properties of the products[9-17]. Studies concerned with theoretical problems, which are solved using heteroadamantanes as model compounds, are being published systematically[18-22]. Bearing in mind also the great practical value[23-26] and physiological activity[27-42] of these compounds, it is useful to survey the new advances in this branch of synthetic organic chemistry.

We classified the literature data on the basis of the formal synthetic schemes rather than the type of heteroatoms. Such treatment makes it possible to discuss simultaneously the synthesis of adamantane heteroanalogues containing various heteroatoms and thus find the genetic relation between these structures. An undoubted advantage of this type of arrangement of data is the possibility of using a formal scheme for the synthesis of heteroadamantane which have not yet been described, containing, for example, rarely encountered heteroatoms.

II. FORMAL SCHEMES FOR THE SYNTHESIS OF HETERO-ADAMANTANE STRUCTURES

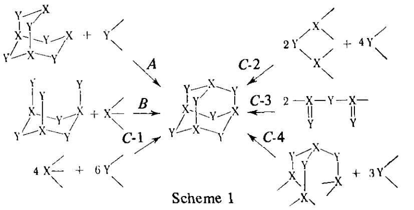
The formal schemes for the synthesis of adamantane heteroanalogues can be divided into several types: (1) synthesis from bicyclic structures; (2) synthesis from monocyclic structures; (3) synthesis from acyclic structures. Furthermore, methods of synthesis based on the transformation of the skeletons of other polycyclic skeletal structures constitute a class on its own to some extent. The data in this review are classified in accordance with these types.

A few words must be said about the nomenclature of heteroadamantanes. According to IUPAC rules[43], the atoms of the adamantane skeleton should be numbered in a sequence such that the heteroatoms have the lowest possible numbers. The general numbering of the skeleton is the same as that adopted for adamantane itself[44,45]. When several heteroatoms of different types are present, the numbering sequence must be as follows: O, S, SE, N, P,. . . , Si, Ge,. . .



When typical synthetic schemes are considered, one must bear in mind the following characteristic of heteroadamantane structures: tervalent and quadrivalent atoms (boron, nitrogen, phosphorus, and silicon) can occupy any position in the adamantane nucleus, while bivalent atoms (oxygen and sulphur) are known *a priori* to be incapable of occupying bridgehead positions. Before oxygen or sulphur can occupy the 1-, 3-, 5-, and 7- bridgehead positions in the adamantane structure, they must be converted into the onium state. For this reason, the introduction of a heteroatom into a bridgehead position is usually fairly specific, while the methods for the introduction of heteroatoms into the 2-, 4-, etc., positions in the adamantane skeleton have much in common.

The most convenient and most frequently employed starting materials for the synthesis of the adamantane skeleton are derivatives of bicyclo[3,3,1]nonane (pathway *A*). The availability of compounds of this series[46,47] and the possibility of extensive modification of the substituents and reactive groups makes this synthetic pathway extremely promising. The method of synthesis from monocylic fragments (pathway *B*) is less general and reduces mainly to the synthesis of adamantanes with heteroatoms in the 1-, 2-, 9-, and 10-positions. Finally, there is a whole series of synthetic approaches to heteroadamantanes based on the condensation of aliphatic compounds (pathways *C*-1–*C*-4). All these variants are presented in Scheme 1.



Scheme 1

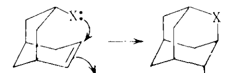
The synthetic pathways *C*-1–*C*-4 can include the formation of mono- or bi-functional compounds at intermediate stages. However, in the present review we shall not consider the detailed mechanisms of such condensations. This would be fairly difficult because their mechanisms are so far unknown in most instances and furthermore a formal treatment makes it possible to give a systematic account of data on the basis of the types of initial structures employed. Such treatment significantly facilitates the search for synthetic pathways to new heteroadamantane structures regardless of the type of heteroatom.

III. SYNTHESIS OF HETEROADAMANTANES FROM BICYCLO[3,3,1]NONANE SYSTEMS

The greatest number of heterocylic systems having the adamantane structure have been synthesised from bicyclo-[3,3,1]-nonane derivatives. This synthetic pathway may be difficult because the synthesis of the initial bicyclic structures is in many cases fairly laborious.

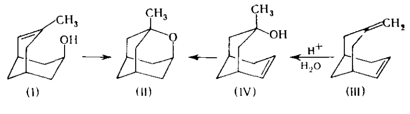
1. Synthesis Involving Multiple Bonds in the Ring

When the bicyclo[3,3,1]non-2-ene molecule contains a functional group in the *endo*-7-position, intramolecular cyclisation via Scheme 2 is possible in principle:



Scheme 2

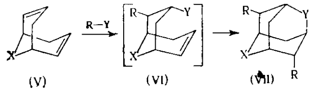
By virtue of steric factors, cyclisation of this type should occur extremely readily and the problem reduces to modifications of the method for the introduction of a double bond or a functional group into the ring or to the synthesis of the bicyclononane skeleton itself. However, examples of cyclisations of this kind are so far known only for adamantane itself[48,49] and for homoadamantane heteroanalogues[50–53]. A characteristic example of reactions of this type is the cyclisation of 7-hydroxy-3-methylbicyclo[3,3,1]non-2-ene (1) to 1-methyl-2-oxa-adamantane (II) in an acid medium[54,55]:



(I) (II) (IV) (III)

The ring closure of the diene (III) to a tricyclic system should be included in the same type of cyclisation, since oxa-adamantane (II) is formed in an acid medium via compound (IV).[56]

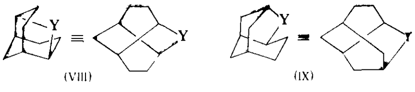
One of the commonest procedures for the introduction of a heteroatom involves electrophilic addition to multiple bonds in the bicyclo[3,3,1]nona-2,6-diene system via Scheme 3:



(V) (VI) (VII)

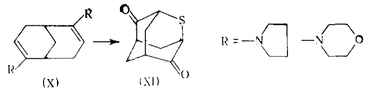
Scheme 3

In practice the reaction product is always a derivative of the adamantane structure (VII) and the intermediate monofunctional derivative of type (VI) cannot be isolated. The reaction is sometimes accompanied by the formation of twistane (VIII) and isoadamantane (IX) derivates[57]:



(VIII) (IX)

The initial diene structure of type (V) is usually synthesised by a method involving the transformation of the functional groups of 3,7- and 2,6-disubstituted bicyclononane derivatives. Dehydrohalogenation[58–60] or dehydration[61] reactions as well as the formation of enol or enamine derivatives from diketones[62,63] are most frequently used. Electrophilic addition to the diene (V) in water proceeds via a mixed addition mechanism and leads to 4,8-disubstituted derivatives (VII). A whole series of mono- and diheteroadamantanes, listed in Table 1, have been obtained on the basis of this reaction. The reaction of the diene (V) with sulphur dichloride proceeds via the same electrophilic addition mechanism. When the 2,6-disubstituted diene (X) is treated with sulphur dichloride, 4,8-dioxo-2-thia-adamantane (XI) is formed. It has been used as the starting material for the preparation of a series of 2-thia-adamantane derivatives[19,64,65]:

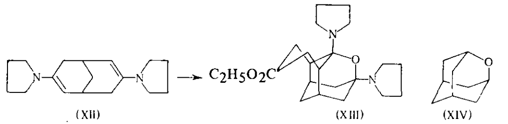


(X) (XI)

Table 1. 4,8-Disubstituted 2,6-diheteroadamantanes of type (VII) synthesised from bicyclo[3,3,1]nona-2,6-diene (V)

X	Y	R	R′	References
CH_2	O	HgOAc, HgI, HgCl, I, Br, OH, H	—	58, 61, 72
CH_2	N—R′	Br, H	H, CH_3, Tos	64, 73–75
CH_2	S	H, OH, Br, Cl, $=CH_2$, =O	—	58, 64
O	N—R′	Br, H	H, Tos	60, 64, 74, 75
O	O	HgOAc, HgI, HgCl, I, Br, H	—	59, 76, 77
O	S, SO_2	Cl, H, OCH_3, OH, OAc	—	57, 59, 76
S	S	Cl, OCH_3, H	—	78
S	Se	Cl	—	69
N—R′	S, O	Cl, Br, H, OH, OAc	$C_6H_5SO_2$, Tos, H, $CO_2C_2H_5$, CHO, CH_3	60, 64, 74, 79

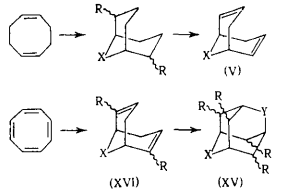
The condensation of the bisenamine (XII) with ethyl bromomethylacrylate leads to the pentacyclic structure (XIII), which is based on the 2-oxa-adamantane skeleton[63]:



(XII) (XIII) (XIV)

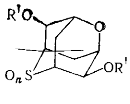
It is noteworthy that the hydration of the diene (V, X = CH_2) with sulphuric acid gives the unsubstituted 2-oxa-adamantane (XIV) in 26% yield[59]. The formation of the dioxa-adamantane (VII, X = Y = O, R = H) as a side product in the synthesis of 2,7-dioxatwistane from 9-oxabicyclo[3,3,1]nonane-2,6-diol has been explained by the same reaction of the diene (V, X = O) with sulphuric acid[66].

The synthesis of 2,6-diheteroadamantanes is based on bicyclic dienes (V) with the heteroatom in the 9-position as the starting compounds. A convenient version of the synthesis of the latter involves reactions based on unsaturated cyclo-octane derivatives via Scheme 4:



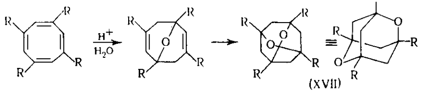
Scheme 4

When cyclo-octatetraene was treated twice with sulphur dichloride, tetrachlorodithia-adamantane (XV, X = Y = S, R = Cl) was obtained[67,68] and the addition of selenium monochloride to the dichlorothia-derivative (XVI, X = S, R = Cl) leads to the thiaselena-adamantane (XV, X = S, Y = Se, R = Cl).[69] A detailed study of the ^1H NMR spectra of oxide derivatives of 2-oxa-6-thia-adamantane (XVII, X = SO_n, Y = O, R = OR′)[78] and also of heteroadamantanes of type (VII, X = O, Y = O or N-Tos; X = N-Tos, Y = CH_2, O, or N-Tos),[61,74] synthesised from *cis*, *cis*-cyclo-octa-1,5-diene, showed that the elementary stage is *trans*-addition, which determines the configuration of the substituted heteroadamantanes obtained:



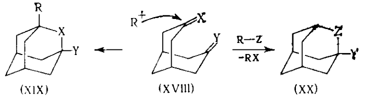
n = 1, R′ = H;
n = 2, R′ = H, Ac .

Treatment of 1,3,5,7-tetra-alkoxycyclo-octatetraene with alcohol containing a small amount of hydrogen chloride leads to the formation of 1,3,5,7-tetra-alkoxy-2,6-dioxa-adamantane (XVII),[70] the structure of which was demonstrated by X-ray diffraction[71].



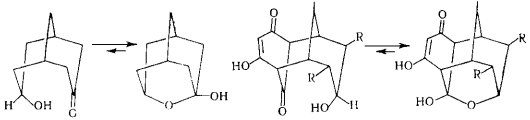
2. Condensation Involving Exocyclic Multiple Bonds

This type of formation of heteroadamantane systems can be represented schematically as follows:



Scheme 5

The basic idea of this scheme consists of the intermediate formation of *endo*-functional derivatives capable of an intramolecular reaction via the second multiple bond. The tendency towards intramolecular cyclisation is also caused by the steric proximity of the fragments at $C_{(3)}$ and $C_{(7)}$. For example, we may note that the ketoalcohol (XXI) exists in the hemiacetal form (XXII).[80] This is true also for more complex polycyclic structures. For example, the derivative of 2-oxa-adamantane (XXIV) is the hemiacetal form of compound (XXIII)[81,83]:

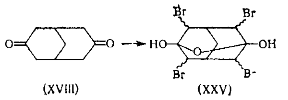


Bicyclononane derivatives with exocylic multiple bonds in the 3- and 7-positions, as in compound (XVIII, X = O or CH_2, Y = O or CH_2), are the most convenient starting compounds for condensations of this type. The difficulty of the method arises from the laborious synthesis of the initial bicyclic structures, which are obtained mainly by the cleavage of the adamantane skeleton[83-87]. A series of 2-oxa- and 2-aza-adamantanes (XIX), listed in Table 2, have been obtained from bicyclic derivatives (XVIII) via Scheme 5.

Table 2. 1,3-Disubstituted 2-heteroadamantanes of type (XIX) synthesised from unsaturated bicyclic compounds (XVIII).

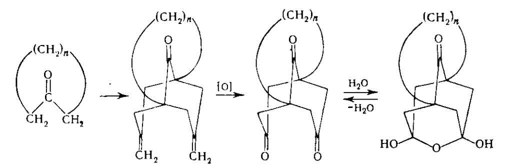
(XVIII)		(XIX)				References
X	Y	X	Y	R	R′	
O	O	O, N—R′	OH, Cl	CH_3, C_6H_5	H, CH_3, Tos, C_6H_5CO	62, 80, 87, 88
O	CH_2	O	CH_3, C_6H_5, CH_2R'	H, OH	HgOAc, I	88—90
O	N—R′	O, N—R′	OH, NHR′	—	H, $NH\overset{O}{\overset{\|}{C}}NHSO_2C_6H_4R'$	89, 90
N—OH	N—OH	N—H	NH_2, OH	—	—	87
O	CHOH	O	CH_3	—	—	91

Bromination of the diketone (XVIII, X = Y = O) in acetic acid with four equivalents of bromine yields 4a, 8a, 9a, 10a-tetrabromo-1,3-dihydroxy-2-oxa-adamantane (XXV). On the other hand, bromination with 4.5 equivalents of trimethylphenylammonium tribromide in CH_2Cl_2 leads to a mixture of 4e, 8e, 9a, 10a-tetrabromo-derivative (XXV) and 2,6-dibromotriasterane-3,7-dione, which are separated chromatographically[92]. The authors assume that the oxa-adamantane system is formed via a tetrabromodiketone stage:



The presence of bromine atoms in both positions adjoining the C=O groups can enhance the electrophilic properties of these groups so much that the hydrated forms are stabilised and the latter can subsequently cyclise spontaneously to the oxa-adamantane system.

A study of the condensation of the cycloalkanones (XXVI, n = 9 or 10) and αα′-dichloroisobutene demonstrated[93] the formation of a considerable amount of the dimethylene derivative (XXVII). The oxidation of the olefin (XXVII) with potassium permanganate followed by treatment with lead tetra-acetate gives a 13% yield of the triketone (XXVIII), which is converted into the oxa-adamantane (XXIX):

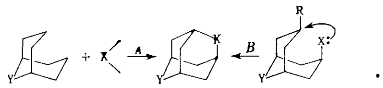


(XXVI) (XXVII) (XXVIII) (XXIX)

The authors concluded that the mobile decamethylene chain not only does not interfere with the formation of the oxa-adamantane system but actually promotes it, since it should favour the double chair conformation in the conformational equilibrium of the bicyclo[3,3,1]nonane system[94].

3. Condensation Without the Involvement of Multiple Bonds and Heteroatoms

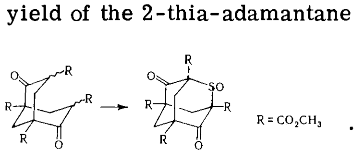
The reactions involving cyclisation to the adamantane structure of initial bicyclo[3,3,1]nonane derivatives without multiple bonds or heteroatoms participating in the formation of a tricyclic system are presented in Scheme 6.



(XXX) (XXXI) (XXXII)

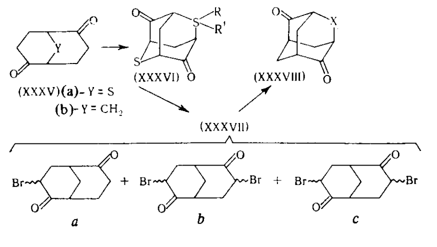
Scheme 6

This scheme (pathway *A*) applies when the so called "Meerwein ester" (XXXIII) reacts with thionyl chloride[82]. This gives rise to a 71% yield of the 2-thia-adamantane system (XXXIV):

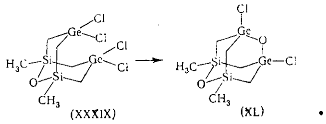


(XXXIII) (XXXIV)

An analogous tricylic system [XXXVI, (RR') = CH_2; R = CH_3, R' = OH or OAc] has been obtained by the reaction of the diketone (XXXVa) with acetic anhydride in a highly acid medium[95]. On bromination with pyridine hydrobromide perbromide, the diketone (XXXVb) gives a mixture of the mono- and di-bromo-derivatives (XXXVII, a–c).[98] On treatment with ammonia in absolute dioxan, 2-aza-adamantane-4,8-dione (XXXVIII, X = NH) was obtained from this mixture of bromo-derivatives:

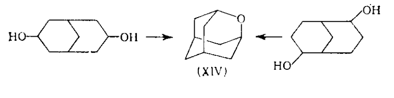


The replacement of ammonia by methylamine leads to the *N*-methyl derivative of 2-aza-adamantane (XXXVIII, X = NCH_3). Reduction of the dibromo-derivative (XXXVIIc) with sodium tetrahydroborate in aqueous alcoholic solutions leads to 2-oxa-adamantane-4,8-diol and, in the presence of catalytic amounts of alkali, to the oxa-adamantane (XXXVIII, X = O).[97] Heteroadamantanes (XL) containing O, Si, and Ge have been obtained via the same pathway *A* by treating the chlorogermane (XXXIX) with water[98]:



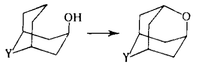
(XXXIX) (XL)

The formation of mono-oxa-adamantane (XIV) from bicyclo[3,3,1]nonane-3,7-diol under the influence of concentrated sulphuric acid is an example of type *B* condensations of bicylic compounds[83,84]. 2-Oxa-adamantane can be obtained by the same pathway from the readily available bicyclo-[3,3,1]nonane-2,6-diol[99,100]. Evidently the formation of 2-oxa-adamantane in the latter case requires a series of hydride shifts:



(XIV)

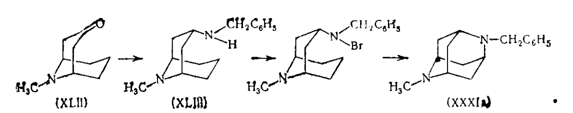
Treatment of the *endo*-alcohol (XLI, Y = CH_2) with lead tetra-acetate in boiling benzene or its oxidation with a mixture of iodine and mercury(II) oxide in carbon tetrachloride give rise to oxa-adamantane (XIV)[101] in yields of 89 and 60% respectively. The *exo*-isomer (XLI, Y = CH_2) is unreactive with respect to lead tetra-acetate and the main product of its oxidation with mercury(II) oxide was the corresponding ketone:



(XLI) (XXXI), X = O

6-Oxa-2-phospha-adamantane (XXXI, X = O, Y = PC_6H_{11}, $\overset{O}{\overset{\|}{P}}CH_2PH$, or $PPhCH_2$)[102] and 6-oxa-2-aza-adamantane (XXXI, X = O, Y = $NCOCH_3$)[103] skeletons have been obtained by a similar method. The attempts to synthesise the oxa-aza-adamantane system by the cyclisation of the benzylamino-derivative (XLI, Y = NCH_2Ph) have been unsuccessful, while refluxing of the acetamido-derivative (XLI, Y = NCH_3CO) in benzene in the presence of lead tetra-acetate leads smoothly to 6-oxa-2-aza-adamantane (XXXI, X = O, Y = $NCOCH_3$). The same heteroadamantane system (XXXI, X = O, Y = NCH_3) was obtained at 85% yield by the acid cyclisation of 7-ethoxy-*N*-methyl-3α-granatanol (XXXII, X = OH, Y = NCH_3, R = OC_2H_5) with hydrobromic acid[104].

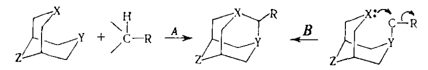
The Hofmann–Löffler reaction was used for the first time in 1973 to synthesise the 2,6-diaza-adamantane system[105]. Reductive amination of the ketone (XLII) in the presence of benzylamine leads to the amine (XLIII), which is converted into the diaza-adamantane derivative (XXXIa) by subsequent bromination and cyclisation in sulphuric acid:



(XLII) (XLIII) (XXXIa)

4. Condensations Involving the Heteroatoms of Bicyclo-[3,3,1]nonane Derivatives

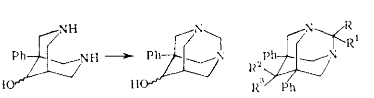
Reactions of this type are used to synthesise mono- and di-heteroadamantanes with heteroatoms in the 1- and 3-positions, which can be represented schematically as follows:



(XLIV) (XLV) (XLVI) .

Scheme 7

Reactions of this kind are used most typically in the synthesis of diaza-adamantane systems (pathway *A*). The simplest instance is the condensation of 3,7-diazabicyclo[3,3,1]nonane (bispidine) (XLIV, X = Y = NH, Z = CH_2) with formaldehyde. The problem of the synthesis of the diaza-adamantanes essentially reduces therefore to the problem of the synthesis of bispidine and similar structures. Likewise the condensation of bispidinol (XLVII) with paraformaldehyde in alcohol yields 1,3-diaza-adamantanol (XLVIII)[106]:

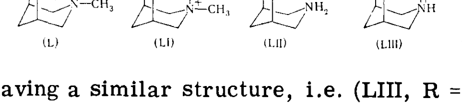

(XLVII) (XLVIII) (XLIX) .

When 1,5-diphenylbispidin-9-ol and 1,5-diphenylbispidin-9-one were treated with the corresponding aldehydes or ketones, a series of biologically active 2-substituted diaza-adamantanes of type (XLIX) were obtained[107] (listed in Table 3).

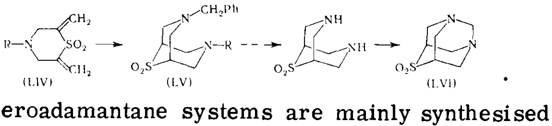
Table 3. 1,3-Diaza-adamantanes (XLIX) obtained by the condensation of bispidine derivatives with formaldehyde[107]

R^2	R^3	R	R^1
H	OH	H, Me, Et	Me, Et, Pr, iso-Pr, Ph, p-$MeOC_6H_4$, 2-furyl, Me, Et, Pr
$(R^2R^3) = O$		H, Me, Et	iso-Pr, Ph, p-$MeOC_6H_4$, 2-furyl, 4,3-$HO(MeO)C_6H_3$

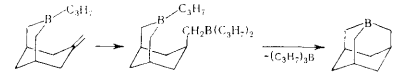
A flattened double chair conformation has been found for *NN'*-dimethylbispidines[108], which promotes the formation of intramolecular hydrogen bonds in salts of bispidine derivatives (for example, perchlorates) and this results in the formation of the adamantane-like structure (L). When *NN'*-dimethylbispidine was treated with methylene iodide, a high yield of diaza-adamantane (LI) was obtained[109]:


(L) (LI) (LII) (LIII) .

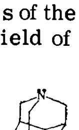
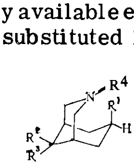
Products having a similar structure, i.e. (LIII, R = H or CH_3), are also obtained when bispidine salts (LII) are treated with formaldehyde and formic acid[110]. 6-Oxa-1,3-diaza-adamantane (XLV, X = Y = N, Z = O, R = H) has been synthesised from diallylamine via the intermediate formation of 9-oxabispidine (XLIV, X = Y = NH, Z = O).[111] The reaction of the diallylamide of benzenesulphonic acid with mercury acetate gives rise to the morpholine system, which is converted into 9-oxabispidine on treatment with ammonia. The condensation of the bispidine derivative with paraformaldehyde leads to the oxadiazo-adamantane (XLV, X = Y = N, Z = O, R = H). The 6-thia-1,3-diaza-adamantane system has been synthesised by an analogous sequence of reactions[112]. The reaction of sulphur dichloride with *NN*-diallybenzene-sulphonamide results in cyclisation to the thiomorpholine system (LIV). Similar cyclisation reactions have been described previously[113]. Subsequent interaction with benzylamine leads to the cyclisation of the thiomorpholine system to the thiobispidine system (LV), which is converted in several stages, involving subsequent condensation with formaldehyde, into 6-thia- 1,3-diaza-adamantane (LVI):


(LIV) (LV) (LVI) .

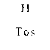
1-Heteroadamantane systems are mainly synthesised via pathway *B* (Scheme 7). Bicyclononane derivatives (XLVI) substituted in the 3- (at the heteroatom) and 7-positions of the bicyclononane molecule are convenient starting materials for this pathway. The synthesis of 1-bora-adamantanes is an example of condensations of this kind. The hydroboration of 7-methylene-3-propyl-3-borobicyclo[3,3,1]nonane (LVII) with tetra-n-propyldiborane leads to compound (LVIII), the cyclisation of which with elimination of 3-propylborane yields 1-bora-adamantane (LIX).[114,115] When compound (LVIII) interacts with pyridine, the pyridine adduct of 1-bora-adamantane is formed[116]. We may note that the geometry of bora-adamantane should simulate the structure of the 1-adamantyl carbonium ion:


(LVII) (LVIII) (LIX) .

The starting compound for the synthesis of the aza-adamantane (LXa) is the 3-azabicyclononane derivative (LXI), synthesised by the condensation of ethyl α-bromomethacrylate or its precursor ββ'-dibromoisobutyrate with the enamine derived from *N*-toluenesulphonylpiperidin-4-one[117] or other *N*-substituted piperidin-4-ones[118,119]. The reduction of the ketoester (LXIa) with lithium tetrahydroaluminate gives the diol (LXId), which is smoothly detosylated under the influence of a mixture of hydrochloric and acetic acids to give 4-hydroxy-1-aza-adamantane (LX, R = OH). Catalytic hydrogenolysis of the readily available ethylene acetal (LXIe) gives a high yield of 2,6-disubstituted 1-aza-adamantane[118]:

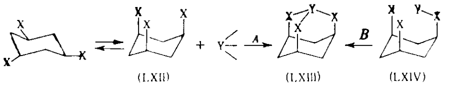
(LX) (a)-R = OH, H, NH_2; R^1 = H;
(b)-R = H; R^1 = CH_2OH

(LXI)	a	b	c	d	e
R^1	CO_2Et	CO_2Et	CO_2Et	CH_2OH	CO_2Et
R^2	$\}=O$	OH	H	OH	
R^3		H	OH	H	
R^4	Tos	Tos	Tos	Tos	CO_2CH_2Ph

.

IV. CONDENSATION AND INTRAMOLECULAR CYCLISATION OF *CIS*, *CIS*-1,3,5-TRISUBSTITUTED CYCLOHEXANES

The general scheme for the synthesis of 2,4,10-triheteroadamantanes involves the condensation of *cis*, *cis*-1,3,5-trisubstituted cyclohexanes with compounds containing a fragment Y capable of condensing with three functional groups at once to form single bonds in accordance with Scheme 8 (pathway *A*):

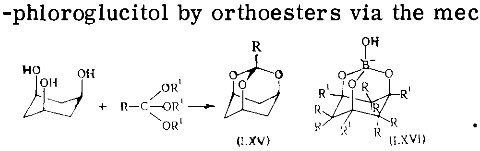


(LXII) (LXIII) (LXIV)

Scheme 8

It is possible to suggest a version of the general scheme where the tervalent component is already combined with one of the functional groups, as shown in Scheme 8 (pathway *B*). Possibly in the synthesis of triheteroadamantanes via pathway *A*, stage *B* is included as an intermediate step and the two versions are indistinguishable. However, it is methodologically useful to distinguish pathway *B*, since it is suitable also for the synthesis of 2,4-diheteroadamantanes.

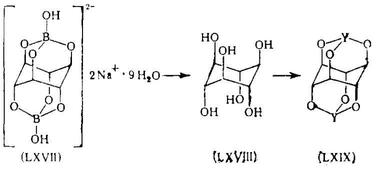
This type of condensation was used for the first time to synthesise the 2,4,10-trioxa-adamantane system (LXIII, X = O, Y = CH).[126] The synthesis involves the esterification of *cis*-phloroglucitol by orthoesters via the mechanism



(LXV) (LXVI)

cis-Phloroglucitol has proved to be a very readily available starting compound and is frequently used in similar syntheses[30,31,121-124]. For example, we may note that its condensation with the tetraethyl ester of orthomalonic acid in the presence of boron trichloride yielded 3-ethoxycarbonylmethyl-2,4,10-trioxa-adamantane (LXV, R = $CH_2CO_2C_2H_5$). Using different condensing agents, a series of trisubstituted trioxa-adamantanes (LXV) have been obtained via a similar mechanism[30,31].

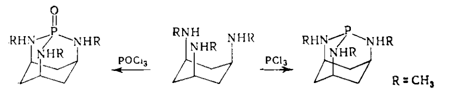
This type of condensation is very suitable for the synthesis of 1-hetero-derivatives of 2,4,10-trioxa-adamantane. In particular, *cis*, *cis*-cyclohexane-1,3,5-triols form stable complexes of type (LXVI) on reaction with sodium metaborate[121]. Evidently this type of condensation is analogous to the well known reaction involving the formation of borate complexes of carbohydrates and polyhydroxy-compounds[125]. It is of interest that *trans*-hexahydroxycyclohexane (scyllitol) (LXVIII) forms a borate complex having the diadamantane structure (LXVII). This reaction is used to isolate scyllitol from natural sources. Scyllitol reacts with triethyl orthoformate in dimethyl sulphoxide (DMSO) to form a polymeric intermediate, which can be converted by pyrolysis into hexaoxadiadamantane (LXIX, Y = CH) in 15% yield. The reaction of compound (LXVIII) with trimethyl phosphite in DMSO or hexamethylphosphoramide yielded diadamantane (LXIX, Y = P)[126]:



(LXVII) (LXVIII) (LXIX)

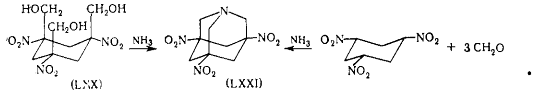
One can also use in this reaction trimethyl phosphate, which reacts with phloroglucitol to give 2,4,10-trioxa-1-phospha-adamantane (LXIII, X = O, Y = P)[122]. The same cyclic system was obtained on treating the *cis*-isomers of cyclohexane-1,3,5-triol derivatives with phosphorus trichloride[121]. The structure of compounds (LXIII, X = O, Y = CH, P, or P=O) has also been studied by ^1H NMR.[127-129]

Similarly to the reaction with *cis*-phloroglucitol, the *cis*-isomer of the triamine (LXII, XR = $NHSO_2C_6H_5$, $NHCH_2C_6H_5$, or $NHCH_3$) condensed with orthoformate in the presence of sulphuric acid to a compound with a 2,4,10-triaza-adamantane structure (LXIII, Y = CH, X = $NSO_2C_6H_5$,[130] $NCH_2C_6H_5$, or NCH_3.[131] Treatment of compound (LXII) with phosphoryl chloride or phosphorus trichloride leads to 2,8,9-triaza-1-phospha-adamantane structures (LXIIIa and LXIIIb):[131]

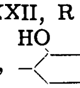
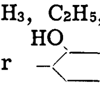


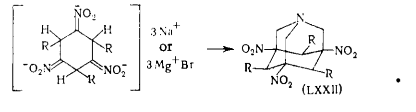
(LXIIIa) (LXIIa) (LXIIIb)

A report[132] of a study of the structure of 1,3,5-trihydroxymethyl-1,3,5-trinitrocyclohexane isomers (LXX) and the synthesis of 3,5,7-trinitro-1-aza-adamantane (LXXI) by the condensation of the triol (LXX) with ammonia in an alkaline medium was published in 1972:



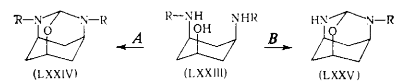
(LXX) (LXXI)

The condensation of 1,3,5-trinitrocyclohexane with ammonia and formaldehyde also led to compound (LXXI). 3,5,7-Trinitro-1-aza-adamantane (LXXI) and a number of its derivatives [LXXII, R = CH_3, C_2H_5, $CH(CH_3)_2$, n-C_4H_9, $CH_2CH(OH)CH_3$, , or ][133] have been obtained by the reduction of 1,3,5-trinitrobenzene with sodium tetrahydroborate or Grignard reagents followed by treatment of the reduction products with formaldehyde and ammonium chloride:

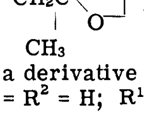


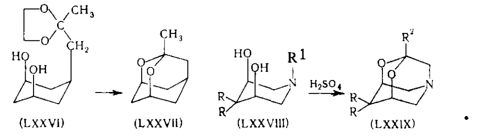
(LXXII)

The condensation of the hydroxyamine (LXXIII) with triethylorthoformate leads to the formation of derivatives of 2-oxa-4,10-diaza-adamantane (LXXIV):[134]



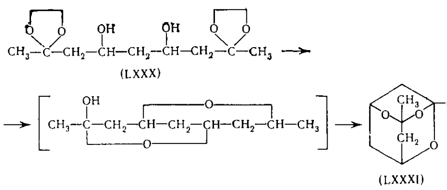
(LXXIV) (LXXIII) (LXXV)

The starting compound (LXXIII) is interesting because its *N*-acyl derivative (R = $COCH_3$) can be converted by intramolecular cyclisation into oxadiaza-adamantane (LXXV) (Scheme 8, pathway *B*). This mechanism can also be illustrated by the following example. Treatment of the ethylene ketal (LXXVI) with sulphuric acid leads to 1-methyl-2,6-dioxa-adamantane (LXXVII)[135] and cyclisation of the *N*-substituted 3,5-dihydroxypiperidine [LXXVIII, R = H, or CH_3, R^1 = $CH_2CH(OC_2H_5)_2$, CH_2Ph, or ] under the influence of sulphuric acid yields a derivative of 4,9-dioxa-1-aza-adamantane (LXXIX, $R^1 = R^2$ = H; R^1 = H, R^2 = CH_3; R^1 = CH_3, R^2 = H)[136]:



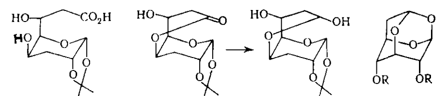
(LXXVI) (LXXVII) (LXXVIII) (LXXIX)

3,5-Dimethyl-2,4,6-trioxa-adamantane (LXXXI) has been obtained by the hydrolysis of the diethylene ketal (LXXX) with a dilute inorganic acid followed by the elimination of water from the non-isolated bicyclohemiketal form[137]:


(LXXX)

(LXXXI)

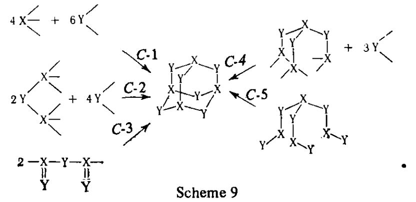
The 2,4,6-trioxa-adamantane system has also been obtained by the intramolecular cyclisation of compound (LXXXIV)[138,139]. On refluxing with molecular sieves in toluene, the ammonium salt of the acid (LXXXII) yields the lactone (LXXXIII), the hemiacetal (LXXXIV) of which is converted into 6-deoxy-*D*-glucodealdoheptose on hydrolysis. 50% of the latter exists in the cyclic trioxa-adamantane form (LXXXV, R = H):


(LXXXII) (LXXXIII) (LXXXIV) (LXXXV)

like *D*-glucuronic acid, 6-deoxy-*D*-glucohepturonic acid is capable of being converted into a lactone[140]. The hemiacetal of this lactone also gives rise to the trioxa-adamantane structure (LXXXV), as shown by ^{1}H NMR.[141,142]

V. SYNTHESIS FROM ACYCLIC COMPOUNDS

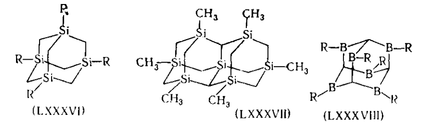
One should note in the first place that almost any heterocyclic system with the adamantane structure can be constructed from acyclic fragments, but the later must contain both atoms capable of occupying the 1-, 3-, 5-, and 7-positions in the adamantane skeleton and bivalent atoms known on *a priori* grounds to be incapable of occupying bridgehead positions. The ratio of the reactants depends on the number of atoms in the initial fragments involved in the construction of the adamantane skeleton. Condensation of this type can therefore be represented by several formal schemes (Scheme 9):



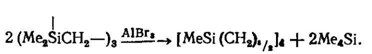
Scheme 9

The simplest initial structures are ammonia and formaldehyde (pathway *C*-1). Their condensation was achieved for the first time in 1860 in the synthesis of hexamethylenetetramine (urotropine or 1,3,5,7-tetra-aza-adamantane)[143], to which the adamantane structure was attributed as early as 1895.[144] The methods of synthesis of urotropine derivatives are not considered in this review, since the chemistry of urotropine constitutes an independent field.

The *C*-2 pathway is frequently followed in the synthesis of sila-adamantanes by the pyrolysis of simple halogenosilanes and silanes with carbon-containing substituents. For example the pyrolysis of tetramethylsilane at 650°C led to the isolation of tetramethyltetrasila-adamantane (LXXXVI, R = Me) from a complex mixture of reaction products[145-149]:


(LXXXVI) (LXXXVII) (LXXXVIII)

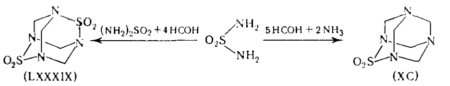
In addition, compound (LXXXVII)[148,150], the structure of which was demonstrated by ^{1}H NMR, was isolated by chromatography. The yield of the tetrasila-adamantane derivative (LXXXVI, R = Me) increased greatly (sometimes to 80%), when 1,3,5-hexamethyl-1,3,5-trisilacyclohexane was introduced into the reaction[151]:


$$2\,(\mathrm{Me_2\overset{|}{S}iCH_2{-}})_3 \xrightarrow{\mathrm{AlBr_3}} [\mathrm{MeSi(CH_2)_{3/2}}]_4 + 2\mathrm{Me_4Si}.$$
(LXXXVI)

Pyrolysis of chlorotrimethylsilane at 700°C leads to a mixture of compounds ranging from fully chlorinated derivatives (LXXXVI, R = Cl) to fully methylated sila-adamantanes (LXXXVI, R = Me), which can be separated chromatographically[149,152]. The tetrachloro-derivative (LXXXVI) was also obtained from chlorotrimethylsilane and tetrachlorosilane in the presence of aluminium chloride at 500°C but in very low yields[153]. The interaction of carbon-containing silanes incorporating Si–Cl groups with $ZnCl_2$ in organic solvents leads to cyclic fluorinated carbon-containing silanes (LXXXVI, R = F) where all the hydrogen atoms can be replaced by chlorine on photochemical chlorination[154]. Bora-adamantanes with a structure of type (LXXXVIII, R = Me) can be obtained via similar reactions on pyrolysis of trimethylboron at 450°C.[155]

Thus pathway *C*-2 is extremely convenient for the synthesis of various tetrasila-adamantanes with structures of type (LXXXVI, R = Cl, Br, or Me) and possibly also structures with heteroatoms such as germanium and tin, when starting compounds having structures containing the $SiCH_2$, CH_2Si, Si_3CH, $GeCH_2$, or $SnCH_2$, etc. fragments are used.

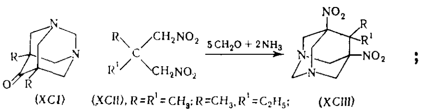
The *C*-3 type of condensation can be illustrated by the synthesis of tetramethylenetetramine disulphone (LXXXIX) on reaction between sulphamide and formaldehyde in proportions of 2 : 4.[156] It is noteworthy that the cyclic disulphone (LXXXIX) is extremely toxic and its action on the central nervous system is five times as potent as that of strychnine[157]:



(LXXXIX) (XC)

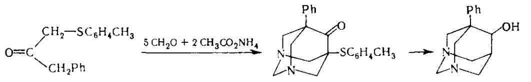
The synthesis of the sulphone (XC) is a kind of combination of pathways *C*-1 and *C*-2 in a single reaction. The condensation of sulphamide, formaldehyde, and ammonia is carried out in an acid medium to give a 90% yield of the sulphone (XC).[158] This type of condensation of acyclic fragments, involved in the construction of the adamantane molecule, constitutes a modified Mannich condensation. The mechanism of the condensation reactions may involve in the initial stages the formation of mono- and bicyclic structures. Although mono- and bicyclic intermediates can be isolated in the Mannich condensation as the main products, depending on the reaction conditions, nevertheless hetero-adamantane structures are usually synthesised without the isolation of the intermediates. We therefore regard this type of condensation as an independent process, bearing in mind the real initial structural units.

The condensation of diethyl acetonedicarboxylate in the presence of ammonium acetate[159] leads to the diaza-adamantane (XCI, R = $CO_2C_2H_5$). The Mannich reaction, which employs dibenzyl ketone and ammonium acetate or dibenzyl ketone, alkylammonium acetate, and ammonium acetate as the starting compounds, gives rise to the diaza-adamantane (XCI, R = Ph) together with a certain amount of bicyclic products[160]:



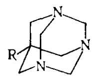
(XCI) (XCII), $R = R^1 = CH_3$; $R = CH_3$, $R^1 = C_2H_5$; $(R, R^1) = -(CH_2)-, -(CH_2)_5-$ (XCIII)

One of the simplest and most convenient methods for the synthesis of 1,3-diaza-adamantane derivatives involves the aminomethylation of compounds containing two active methylene groups with formaldehyde and ammonia salts of weak acids. Thus 2,2-dialkyl-1,3-dinitropropanes (XCII) condense with formaldehyde and ammonium acetate in the presence of ammonium carbonate to form substituted 1,3-diaza-adamantanes (XCIII).[161] Tolylthiophenylacetone is converted by a similar reaction into the diaza-adamantane (XCIV), which is easily reduced by Raney nickel to compound (XLVIII).[105]



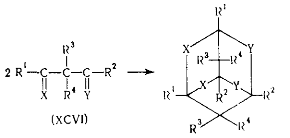
(XCIV) (XLVIII)

The starting compounds used as structural units in the synthesis of substituted 1,3,5-triaza-adamantanes (XCV, R = NO_2 or NH_2) are nitromethane, paraformaldehyde and ammonium acetate[162].



(XCV)

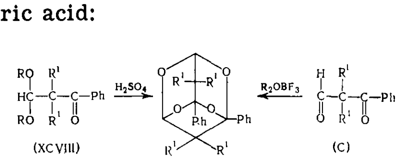
The condensation of β-dicarbonyl compounds and their thioanalogues has a great scope for the synthesis of polyheteroadamantanes. Reactions of this type can be represented schematically as follows:



(XCVI) (XCVII)

Depending on the nature of X and Y, a number of heteroadamantane structures can be synthesised by the "dimerisation" of the initial dicarbonyl compounds or by condensation with other β-dicarbonyl compounds.

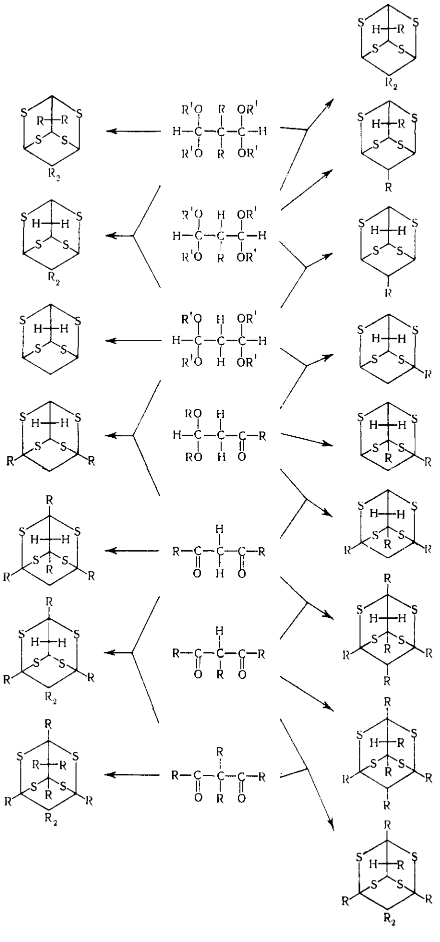
The synthesis of α-formylisobutyrophenone (XCVI, X = Y = O, R^1 = Ph, R^2 = H, $R^3 = R^4$ = Me)[163] from the acetal (XCVIII, R = C_2H_5, R^1 = CH_3) was described in 1959. It was later established[164] that the compound, to which the structure of α-formylisobutyrophenone had been erroneously attributed in the previous study, is in fact the dimer of this aldehyde. The tetraoxa-adamantane structure (XCIX, R^1 = Me) was proposed for it on the basis of spectroscopic data. It was found that the dimer (XCIX) is obtained in almost quantitative yield when the acetal (XCVIII) is treated with 80% sulphuric acid:



(XCVIII) (XCIX) (C)

The dimerisation of certain β-dicarbonyl compounds in the presence of boron triluoride-ether or zinc chloride in glacial acetic acid leads to only slight yields of tetra- and penta-methyl derivatives of tetraoxa-adamantane, the structures of which have been identified by mass spectrometry. In contrast to this, the dimerisation of the ketoaldehyde (C) leads to an almost quantitative yield of tetraoxa-adamantane (XCIX).[165] This type of dimerisation is also characteristic of thioanalogues[166]. All possible versions of the synthesis of polythia-adamantanes are most clearly illustrated by Scheme 10 of Olsson and Almqvist[166], which is reproduced here.

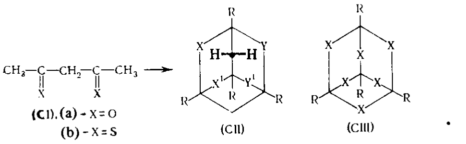
The Syntheses of 2,4,6,8-Tetrathia-adamantane Derivatives[166]



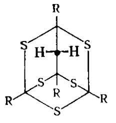
Scheme 10

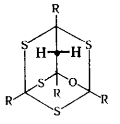
In a strongly acid medium in the presence of hydrogen sulphide, β-diketones, and particularly pentane-2,4-dione (CIa) are converted into derivatives of tetrathia-adamantane (CII, X = Y = X^1 = Y^1 = S) and its mono-oxa- (X = O), dioxa- (X = Y = O), and trioxa-analogues (X = Y = Y^1 = O)

(CII, R = Me).[167] The main product of the reaction of dithioacetylacetone (CIb) was a tetrathia-adamantane (CII, X = Y = X^1 = Y^1 = S, R = Me).[168] The selenium analogue (CII, X = Y = X^1 = Y^1 = Se) was synthesised for the first time in 1969[169] by passing hydrogen selenide through a solution of pentane-2,4-dione in glacial acetic acid in the presence of zinc chloride. In addition the hexaselena-adamantane (CIII, X = Se) was isolated from the mixture of reaction products.


(CI), (a) - X = O
(b) - X = S
(CII) (CIII)

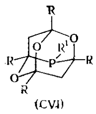
Thiocarboxylic acids and their salts have been used as convenient substitutes of hydrogen sulphide in the synthesis of oxathia-adamantanes. The reaction of β-dicarbonyl compounds with thioacetic acid was carried out for the first time by Brändström[170]. Apart from the tetrathia-adamantane (CII), he obtained two substances, which he regarded without proof as its oxa-analogues (CII, X = O and X = Y = O). The same reaction of β-dicarbonyl compounds (XCVI, X = Y = O; X = Y = S; X = O, Y = S) with thioacetic acid in the presence of zinc chloride led to the synthesis of tetrathia-adamantanes (XCVII), pentathia-adamantanes (CIV), and hexathia-adamantanes (CIII, X = S) in proportions determined by the molar ratios of the initial reactants. Mono-, di-, and tri-oxa-analogues of compound (CII) and the oxatetrathia-adamantane (CV, R = Me) are formed simultaneously[171].

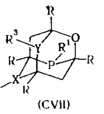

(CIV)

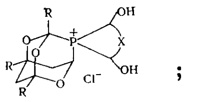

(CV)

Thus β-dicarbonyl compounds react with hydrogen sulphide or thiocarboxylic acids to give isomeric mixtures of thia- and oxathia-adamantanes[2,170], which can be separated by preparative gas–liquid chromatography (GLC) and identified by mass spectrometry[166,172–174].

Using phosphine or primary substituted phosphines instead of hydrogen sulphide, it is possible to obtain by a similar reaction phosphorus analogues having structures of type (CII, X = Y = Y^1 = O, X^1 = P)[175] as well as a series of tetra-alkyl-substituted 2,6,9-trioxa-10-phospha-adamantanes (CVI).[176] By varying the amounts of phosphine or primary substituted phosphine taken for the reaction with an alkyl-β-diketone, it is possible to obtain a series of compounds with a structure of type (CVII):


(CVI)


(CVII)


(CVIII), R = Me, X = –(CH$_2$)$_2$–, –(CH$_2$)$_3$–;
R = CF$_3$, X = –CH$_2$(CHOMe)CH$_2$– ;

where X and Y may be oxygen or phosphorus[177]. Thus, when two equivalents of the β-diketone react with one equivalent of phosphine, compound (CVII, X = Y = O) is the product; the reaction with two equivalents of phosphine yields the oxaphospha-derivative (CVII, X = P, Y = O) and the reaction with three equivalents of phosphine gives rise to the phospha-derivative (CVII, X = Y = P). The compounds obtained in this way are listed in Table 4.

The condensation of secondary substituted phosphines with aldehydes (for example glutaraldehyde) leads to structures of type (CVI), (CVII), and (CVIII).[178] The reaction of α-aminovinyl ketone with hydrogen sulphide leads to the polyheteroadamantane (CIX),[179] the positions of the N, O, and S atoms in which were determined by spectroscopic methods:

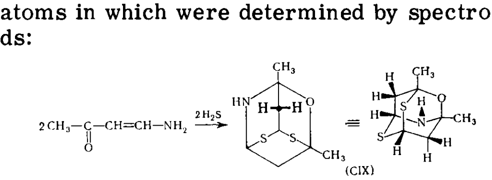
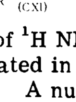

(CIX)

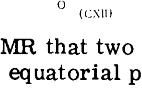
Table 4. Heteroadamantanes with a structure of type (CVII).[177]

X	Y	R	R^1	R^2	R^3
O	O	Me	H, iso-Bu, Octyl, Pr	—	—
O	O	trifluoromethyl	R^1 = R^2 = tris-(2-hydroxyethyl)		
O	O	Pr	dodecyl	—	—
O	O	1,5-diethyl-3,7-dimethyl	benzyl	—	—
O	O	Bu	2-carboxyethyl	—	—
P	O	Me, Et	R^1 = R^2 = bis-(2-cyanoethyl), allyl, cyclohexyl, bis-(*p*-chlorophenyl)		—
P	P	Me	Ph	Ph	Ph
P	P	trifluoromethyl	R^1 = R^2 = tris(2-hydroxyethyl)		H

Synthetic schemes for the preparation of heteroadamantanes via pathway *C*-4 are based on the use as starting compounds of trifunctional derivatives containing in their structure both atoms capable of occupying bridge-positions and atoms occupying the 2-, 4-, and other analogous positions in the adamantane skeleton. Thus the initial fragment already contains seven atoms needed for the construction of the adamantane skeleton. The missing three units are introduced by condensation or intramolecular cyclisation from the substituents present in the initial molecule (see Scheme 9, pathway *C*-5). The triaza-adamantane structure (CXI, R = Me, R^1 = 2-C$_5$H$_4$N) was demonstrated in 1967 for the product of the condensation of tri(aminomethyl)methane (CX, R = CH$_3$, R^1 = NH$_2$) with piperidine-2-aldehyde[180]:

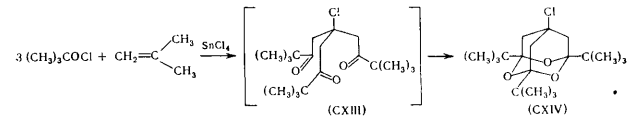
RC(CH$_2$R^1)$_3$
(CX)


(CXI)


(CXII)

It was shown with the aid of ^{1}H NMR that two pyridyl groups in compound (CXI) are located in equatorial positions and one is in an axial position. A number of mono-substituted derivatives of compound (CXI) with the substituents R = H and R^1 = NO$_2$, NH$_2$, HNOH, N(CH$_3$)$_3$, HNCOCH$_3$, HNCOPh, or HNCH$_2$C(NO$_2$)(CH$_3$)$_2$ have been obtained[181] from tri-(hydroxymethyl)nitromethane (CX, R = NO$_2$, R^1 = OH) ammonia, and formaldehyde. Oxaphospha-adamantane derivatives of type (CXII, X = N, P = O) are formed on intramolecular degradation of nitrilotrimethylenephosphonic acid N(CH$_2$.PO$_3$H$_2$)$_3$ or OP(CH$_2$PO$_3$H$_2$)$_3$ by acetic anhydride[182].

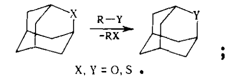
A new type of triacylation in the reactions of pivaloyl halides with isobutene was discovered in 1972.[183] In the presence of tin tetrachloride, this reaction gives rise to the trioxa-adamantane derivative (CXIV), which is probably formed via the triketone (CXIII). The latter is apparently unstable and is spontaneously converted into compound (CXIV):


(CXIII) (CXIV)

The data presented show that the pathways to the synthesis of heteroadamantanes from acyclic compounds are extremely varied and numerous and constitute a large field in the synthesis of various heteroanalogues of adamantane.

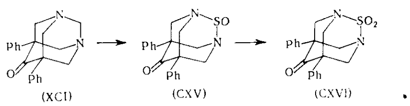
VI. SYNTHESIS BY THE TRANSFORMATION OF POLYCYCLIC STRUCTURES

So far there are few instances in the literature of the formation of heteroadamantane derivatives as a result of the transformation of the skeletons of other polycyclic molecules. However, this method appears fairly promising bearing in mind the advances in the synthesis of a wide variety of polycyclic and skeletal structures. One of the methods formally resembles the Yur'ev reaction[184] (Scheme 11):

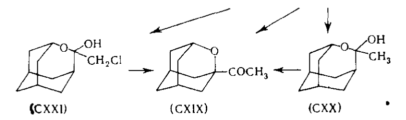


Scheme 11

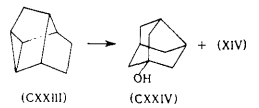
Reactions leading to the substitution of the heteroatom in rings are known also for bicyclo[3,3,1]nonane systems[185–187]. The formation of thiadiaza-adamantane (CXV) from diaza-adamantane (XCI)[188] by treating the latter with $SOCl_2$ in anhydrous pyridine is an example of reactions of this kind involving adamantane structures:



A new pathway to the synthesis of the 2-oxa-adamantane system from derivatives of 2-substituted adamantanols was discovered in 1971.[189] When 2-methyladamantan-2-ol (CXVII, R = Me) was treated with lead tetra-acetate in the presence of iodine, the oxahomoadamantane derivative (CXVIII) was obtained. The di-iodoether (CXVIII) is readily decomposed by dilute hydrochloric acid in DMF to the oxa-adamantane derivative (CXIX). The ketone (CXIX) was also obtained from both homoadamantanes (CXX) and (CXXI) by treatment with iodine in the presence of hydrogen chloride in DMF. Treatment of the adamantanol (CXVII, R = H) with a mixture of yellow or red mercury(II) oxide and iodine, the reaction system being heated or irradiated, leads to a mixture of unsubstituted 2-oxa-adamantane (XIV), and the adamantanone (CXXII).[190] The ratio of the reaction products depends on the molar ratios of the adamantanol, mercury(II) oxide, and iodine and on the reaction temperature:



The unsubstituted oxa-adamantane (XIV) has also been obtained in a low yield (10%) in the reaction of deltacyclane (CXXIII) with concentrated sulphuric acid. Depending on the conditions, the main reaction product is 1-noradamantanol (CXXIV) or 2-noradamantanol[191]:



During the preparation of the manuscript for the press and while it remained with the editors, a number of studies have been published on the synthesis[192–201], properties[202–205], and structure[206–207] of heteroadamantanes containing between one and five heteroatoms in the adamantane structure.

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Methods of Synthesis and Properties of Allylboranes

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The methods of synthesis and chemical properties of allyl derivatives of boron of different types and their applications in organic chemistry, including their use for the synthesis of 1-bora-adamantane and adamantane compounds, are discussed. The bibliography includes 148 references

CONTENTS

I. INTRODUCTION

Studies on the chemical properties of organic boron compounds in recent years have led to the discovery of an increasing number of new fields of application of these substances in organic syntheses. Methods of synthesis based on organoboranes have greatly extended the scope of the applications of organometallic reagents in preparative chemistry, usefully supplementing the available synthetic procedures involving organic derivatives of magnesium, zinc, and alkali metals.

Allyl derivatives of boron, which are highly reactive and exhibit a specific behaviour in relation to different classes of organic compounds, are particularly promising as synthetic reagents. A characteristic feature of triallylborane and some of its analogues is their ability to exist in a state of permanent allyl rearrangement, which takes place at different rates, depending on the nature of the compound and temperature. The high reactivity of allylboranes is manifested in their reactions with water, alcohols, and amines, which occur even at room temperature; this distinguishes them sharply from trialkylboranes, which react with the same substances only at elevated temperatures. Allylboranes react with aldehydes, ketones, quinones, and nitriles like organometallic compounds, their use for synthetic purposes having in many instances considerable advantages compared with magnesium and other metal compounds[1].

A specific feature of allylboranes is their tendency to react with unsaturated compounds. Their reactions with acetylenic and allenic compounds lead to 3-borabicyclo[3,3,1]nonene and 3-borabicyclo[3,3,1]nonane systems, on the basis of which it proved possible to develop a stereospecific method for the synthesis of compounds of the cyclohexene and cyclohexane series, to synthesise unique 1-bora-adamantane systems, and to devise a novel method for the synthesis of adamantane derivatives.

II. METHODS OF SYNTHESIS

Triallylborane was obtained for the first time in 33% yield by the reaction of triallyl borate and allylmagnesium bromide[2]. Triallylborane is also formed from allylmagnesium bromide and n-butyl metaborate[3]. The reaction between allylmagnesium bromide and boron trifluoride-ether constitutes a preparative method for the synthesis of triallylborane[3]:

$$3\,C_3H_5MgBr + BF_3 \rightarrow (C_3H_5)_3B + 3\,MgBrF.$$

The reaction can be carried out in a single stage by adding a mixture of allyl bromide and boron trifluoride-ether to magnesium in an ethereal medium[4,5].

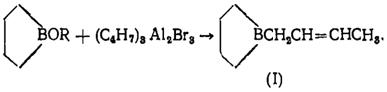
When allylmagnesium chloride and boron trifluoride-ether are used, the yield of triallylborane is 10–47%.[4,6] Allylmagnesium chloride and methyl borate may be used to synthesise triallylborane[7]. Triallylborane can be obtained most conveniently from allylaluminium sesquibromide and n-butyl borate or boron trifluoride-ether[8]:

$$(C_3H_5)_3Al_2Br_3 + BF_3 \xrightarrow[78\%]{} (C_3H_5)_3B + AlF_3 + AlBr_3\ .$$

Tricrotylborane in 75% yield[9] and tri-(2-methylallyl)-borane[10] have been synthesised by the last method.

Mixed organoboranes containing one or two allyl groups are obtained by treating the corresponding acid esters with allyl derivatives of magnesium or aluminium.

1-Crotylboracyclopentane (I) has been synthesised from 1-n-butoxyboracyclopentane[11] or 1-methoxyboracyclopentane[12] and crotylaluminium sesquibromide:



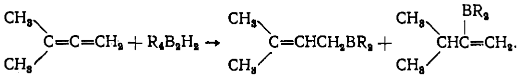
(I)

1-Allylboracyclopentane has been obtained by treating 1-alkoxyboracyclopentane with allylmagnesium bromide or allylaluminium sesquibromide[13]. Dialkylallylboranes[14], alkyldiallylboranes[14], and allyldiarylboranes[15] can be synthesised by this method from dialkylborinic, alkylboronic, or diarylborinic acid esters.

Dialkylallylboranes are also formed when esters of dialkylthioborinic acids are treated with triallylborane[16]:

$$(C_2H_5)_2BSC_6H_{13} \xrightarrow{(CH_2{=}CHCH_2)_3B} (C_2H_5)_2BCH_2CH{=}CH_2.$$

Mixed dialkylallyl compounds of boron can be likewise obtained by adding tetra-alkyldiboranes to allenic hydrocarbons. Dialkyl-(3-methylbut-2-en-1-yl)boranes (II) with an admixture of about 10% of the isomeric compounds (III) have been synthesised by this method[17]:



$$(CH_3)_2C{=}C{=}CH_2 + R_4B_2H_2 \rightarrow (CH_3)_2C{=}CHCH_2BR_2 + (CH_3)_2CHC(BR_2){=}CH_2.$$

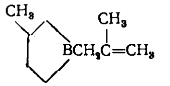
90% (II) 10% (III)

A number of acylic[18] and cyclic[19,20] allenic hydrocarbons have been hydroborated with tetra-(3-methylbut-2-yl)-diborane; the reaction products, containing a mixture of the corresponding substituted dialkylallylboranes and dialkylvinylboranes, were oxidised with hydrogen peroxide.

Alkyldiallylboranes can be obtained by the symmetrisation of dialkylallylboranes. Thus, on being heated above 100°C, diethyl-(3-methylbut-2-en-1-yl)borane is converted into a mixture of triethylborane, ethyldi-(3-methyl-but-2-en-1-yl)borane, and tri-(3-methylbut-2-en-1-yl)borane, which can be separated by fractional distillation[17].

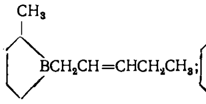
When a 5 : 1 mixture of buta-1,4-diene and diborane reacts in an ethereal medium, a low yield is obtained of a mixture of unsaturated compounds having the composition $C_8H_{15}B$ [together with di-(1-boracyclopentylbutanes)], which consists almost entirely of 1-crotylboracyclopentane[12,21].

The hydroboration of isoprene (using the ratio hydrocarbon : B_2H_6 = 6 : 1) leads to a mixture of 1-alkenyl-3-methylboracyclopentanes [together with di-(3-methylboracyclopentyl)pentanes], which consists to the extent of about 60% of 3-methyl-1-(2-methylbut-2-en-1-yl)boracyclopentane (IV):[22]

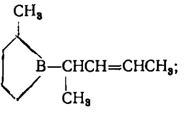


(IV)

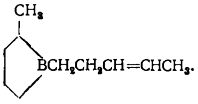
Hydroboration of piperylene yields a mixture of 1-alkenyl-2-methylboracyclopentanes containing about 35% of 2-methyl-1-(pent-2-en-1-yl)boracyclopentane (V), 15% of 2-methyl-1-(pent-3-en-2-yl)boracyclopentane (VI), and 50% of 2-methyl-1-(pent-3-en-1-yl)boracyclopentane (VII):[22]



(V)



(VI)



(VII)

Allyl derivatives of boron with oxygen-containing and other functional groups at the boron atom can be obtained by various methods. A general and preparatively convenient method of synthesis of compounds of this type is based on reactions of triallylboranes, which are highly reactive in relation to different reagents. Allylboronic acids and their esters are formed when allylboranes are treated with water or alcohols at room temperature. Thus triallylborane reacts with water to form allylboronic acid, which is isolated as its anhydride on distillation[3]. Studies on reactions of 1-crotylboracyclopentane[11] and tricrotylborane[9] with water, which lead to the formation of but-1-ene and respectively to 1-hydroxyboracyclopentane and crotylboronic acid established that the protonolysis of the boron–carbon bond takes place with allyl rearrangement. The n-butyl ester of diallylborinic acid can be obtained from triallylborane by treating it with one equivalent of n-butyl alcohol. n-Butyl diallylborinate reacts with n-butyl alcohol to form di-n-butyl allylboronate[3].

When methyl alcohol reacts with diallylborane, the reactants being in proportions of 1 : 1, the dimethyl ester of allylboronic acid is obtained, and not the methyl ester of diallylborinic acid, part of the initial triallylborane being recovered unchanged. This can be explained by the fact that the $(C_3H_5)_2BOCH_3$ formed initially undergoes rapid symmetrisation to $(C_3H_5)B(OCH_3)_2$ and $(C_3H_5)_3B$.[3]

Diethyl[23], di-n-propyl[24,25], di-n-butyl, diallyl, dibenzyl, and diphenyl[24] esters of allylboronic acid have been obtained by treating triallylborane with the corresponding alcohols. Tricrotylborane reacts vigorously with methanol at room temperature to form the methyl ester of dicrotylborinic acid and but-1-ene (98%) with a small admixture of but-2-ene (2%) when the initial reactants are taken in equimolar proportions[9]. Thus the alcoholysis of the B–C bond in allyl derivatives of boron takes place with allyl rearrangement.

In order to convert tricrotylborane into the dimethyl ester of crotylboronic acid, the borane must be heated with methanol[9]. The dimethyl ester of allylboronic acid has been synthesised by treating trimethyl borate with allylzinc or allylaluminium compounds[26]. The reaction of crotylmagnesium bromide and methyl borate with subsequent hydrolysis and transesterification of reaction products with n-hexyl alcohol leads to a mixture of di-n-hexyl esters of 1-methylallylboronic and crotylboronic acids in proportions of 77 : 23, with a 44% overall yield[27]. When crotyl-lithium is used, only the ester of crotylboronic acid is obtained (36%). On standing (for several weeks) or in the presence of magnesium bromide (for 18 h at 55°C), the ester of 1-methylallylboronic acid is slowly converted into the ester of crotylboronic acid. The reaction of hex-2-en-1-ylmagnesium bromide with methyl borate leads to the esters of hex-1-en-3-ylboronic and hex-2-en-1-ylboronic acids in proportions of 86 : 14.[27]

According to patent data[28], the dipentyl ester of allylboronic acid is formed when triallyl borate, allyl bromide, and sodium react with subsequent esterification by pentyl alcohol. A mixture of cyclic esters of allylboronic and isopropenylboronic acids in proportions of 66 : 14 is obtained when allene is heated for a long time at 130°C with 4,4,6-trimethyl-1,3,2-dioxaborinane[29].

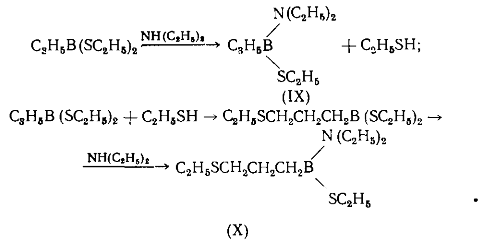
A simple method for the synthesis of dimethyl allylboronate involves heating a 1 : 2 mixture of triallylborane with methyl borate[30]. It has been established by ^{1}H NMR that a 4 : 1 equilibrium mixture of allylboronic and diallylborinic acid esters is obtained from an equimolar mixture of triallylborate and methyl borate, while the proportions of the esters obtained from an initial 2 : 1 mixture are 1 : 2.3.[31] When triallylborane is heated with triisobutyl borate, di-isobutyl allylboronate is obtained[8].

Allylboranes serve as starting materials for the synthesis of allylic thioacids. Triallylborane reacts with ethanethiol at –15°C, the ethyl ester of diallylthioborinic acid and propene being formed from equimolar amounts of the initial reactants[32,33]. When two equivalents of ethanethiol are used, the main reaction product is the diethyl ester of allylthioboronic acid; in addition, the ethyl esters of diallylthioborinic and 3-ethylthio-n-propylthioboronic acids (VIII) are obtained. The latter acid is formed as a result of the addition of ethanethiol to the ester of allylthioboronic acid:

$$(C_3H_5)_3B + C_2H_5SH \xrightarrow[-C_3H_6]{} (C_3H_5)_2BSC_2H_5 \xrightarrow{C_2H_5SH} \underset{\text{(VIII)}}{C_2H_5SCH_2CH_2CH_2B\,(SC_2H_5)_2}.$$

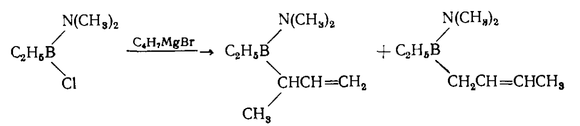
The synthesis of the ethyl esters of diallylthioborinic and allylthioboronic acids has also been described[25].

Like the esters of dialkylthioborinic and alkylthioboronic acids[34–37], those of allylthioboronic acids react readily with various substances. When diethyl allylthioboronate is treated with ammonia, *BBB*-triallylborazole is formed, the reaction with n-butylamine yields allyl-(n-butylamino)-borane, and the reaction with diethylamine leads to the ethyl ester of allyl(diethylamino)thioborinic acid (IX) and to the ethyl ester of (diethylamino)-3-ethylthiopropylthioborinic acid (X):[33]



Allyl-containing amino-derivatives of boron can be obtained from allylboranes. Triallylborane reacts with ammonia and primary and secondary amines to form adducts, which are smoothly converted into diallylaminoborane or its *N*-alkyl derivatives on heating to 100–130°C.[3,38] Diallylaminoborane and alkylaminodiallylboranes have been synthesised by this method[25].

When chloro(ethyl)dimethylaminoborane reacts with crotylmagnesium bromide, a mixture of but-1-en-3-yl-(ethyl)dimethylaminoborane (XI) and but-2-en-1-yl(ethyl)-dimethylaminoborane (XII) is obtained in proportions of 65 : 35:[39]



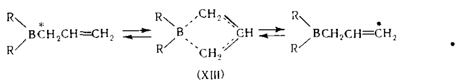
Compound (XI) is comparatively stable at room temperature, but isomerises to compound (XII) at 150°C. The reaction of chlorobis(dimethylamino)borane with crotylmagnesium bromide gives rise to a mixture of but-1-en-3-ylbis(dimethylamino)borane and but-2-en-1-yl-bis(dimethylamino)borane (84 : 16).[40]

Allyldichloroborane is formed when BCl_3 is heated with tetra-allyltin[41].

III. THE PERMANENT ALLYL REARRANGEMENT IN ALLYL DERIVATIVES OF BORON

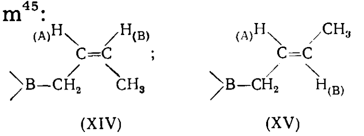
^{1}H NMR studies of triallylborane led to the detection in the latter of a permanent allyl rearrangement[42–44], the activation energy for which proved to be 10 ± 1 kcal mole^{-1}.

The reversible exchange of CH_2 groups in allyl derivatives of boron proceeds via a transition state (XIII) with symmetrically distributed hydrogen atoms in the CH_2 groups relative to the [boron] atom and equivalent B–$\overset{*}{C}$ and B–C bonds.

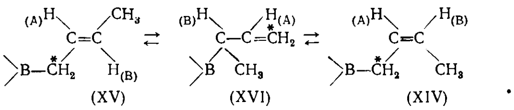


The specific features of the chemical behaviour of triallylborane are undoubtedly associated with the permanent allyl rearrangement occurring in it.

The study of the ^{1}H NMR spectra of tricrotylborane using proton–proton double resonance at frequencies of 60 and 100 HMz shows that this compound exists as a mixture of *cis*- (XIV) and *trans*-isomers (XV) of the but-2-enyl form[45]:



In contrast to triallylborane, there is no permanent allyl rearrangement in tricrotylborane at room temperature. The proton spectrum of the $-CH_{(A)}=CH_{(B)}$ system, obtained using proton–proton double resonance, shows that *trans*-tricrotylborane predominates in the mixture (J_{AB} = 15.0 Hz), its content at room temperature amounting to 70%. The form of the ^{1}H NMR spectrum of tricrotylborane above 150°C indicates the reversible interconversion of the *cis*- and *trans*-isomers at such a rate that the chemical shift and the spin–spin interaction constants of the $H_{(A)}$ and $H_{(B)}$ protons (J = 14 Hz) are averaged. The observed interconversion evidently proceeds via a stage involving the isomerisation of the but-2-enyl form of tricrotylborane (XV) to the but-1-enyl form (XVI), in which there is free rotation about the $H_{(A)}-C-CH_{(B)}$ bond, ensuring the conversion into the *cis*-form of tricrotylborane (XIV):



The interconversions (XV) ⇌ (XVI) and (XVI) ⇌ (XIV) proceed via a transition state of type (XIII).

The study of the ^{1}H NMR spectra of tri-(2-methylallyl)-borane showed[10] that there is a permanent allyl rearrangement in this compound too, occurring more readily than in triallylborane. Thus, at 100°C the rate of rearrangement is 5709 s^{-1}, while in triallylborane at the same temperature it is 2421 s^{-1}. The activation energy for the rearrangement is 9.8 ± 0.5 kcal mole^{-1}.

The permanent allyl rearrangement in tri-(3-methyl-but-2-en-1-yl)borane, 1-allyl-2-(but-2-en-1-yl)5-chloromethylene-4,4-dimethylcyclopentane[46], and 3-allyl derivatives of the 3-borabicyclo[3,3,1]non-6-ene series[47] has been studied by ^{1}H NMR. Permanent intermolecular allyl rearrangements have been detected by ^{11}B and ^{1}H NMR in the exchange reactions of triallylborane, tricrotylborane, and tri-(2-methylallyl)borane with borates[48] and alkyl thioborates[49]. The influence of the permanent allyl rearrangement on the parameters of the NMR spectra of certain allyl derivatives of boron has been studied[50].

IV. CHEMICAL PROPERTIES

1. Capacity for Complex Formation

Triallylborane forms complexes with pyridine[23,51], α-picoline, trimethylamine[51], and diethylamine[38]; a complex of tricrotylborane with pyridine is known[9].

The capacity of triallylborane for complex formation has been studied by ^{1}H and ^{11}B NMR and by boron–proton double resonance[51]. The heats of dissociation of the adducts of triallylborane with trimethylamine, pyridine, 2-methylpyridine, and 3-methylpyridine are respectively 20.6, 25.1, 19.1, and 26.2 kcal mole^{-1}. Reactions involving the substitution of one ligand by another in triallylborane complexes have been investigated by ^{1}H NMR [51] and it has been established that exchange between the free amine and the amine bound in the complex takes place in amine solutions of triallylborane complexes. Tri-(2-methylallyl)borane has a smaller capacity for complex formation than triallylborane[10].

The oxidation of the triethylamine complex of tricrotylborane in an excess of the amine with hydrogen peroxide leads to crotyl alcohol with an admixture of only 2% of

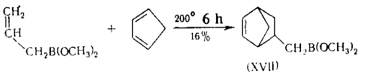
1-methylallyl alcohol, i.e. the oxidative cleavage of the B–C bond takes place without allyl rearrangement[10].

2. Reactions with Organometallic Compounds and Certain Other Reagents

Allyl-lithium adds to triallylborane with formation of lithium tetra-allylborate[52]. Triallylborane, tri-(2-methylallyl)borane, and tricrotylborane enter into exchange reactions with dimethylzinc[53–55] and dimethylcadmium[55,56] with formation of trimethylborane and the corresponding diallyl derivatives of zinc and cadmium. Vanadium tetrachloride forms BCl_3 and allylvanadium trichloride on reaction with triallylborane.

Di-n-butyl allylboronate combines with dichloromethylsilane in the presence of chloroplatinic(II) acid with formation of an ester of 3-methyldichlorosilylpropylboronic acid[58]. In the presence of chloroplatinic(II) acid, triethylsilane adds to the allylboronate ester with much more difficulty. Triethylgermane and triphenylgermane add to dimethyl allylboronate[59] at the double bond of the allyl group linked to $B(OR)_2$ much more readily than to olefinic hydrocarbons and their derivatives having functional groups in the γ-position. The latter substances combine with triethylgermane only in the presence of H_2PtCl_4, while the addition of triethylgermane to the allylboronate ester takes place without catalyst at 110–190°C and leads to the formation of the dimethyl ester of 3-triethylgermylpropylboronic acid in a high yield.

Allylboronate esters are involved in diene condensation with cyclopentadiene and its chloro-derivatives[60]. Dimethyl allylboronate condenses with cyclopentadiene only at a high temperature, forming the ester of *endo*-2-{bicyclo[2,2,1]hept-5-en-1-yl}methylboronic acid (XVII):



(XVII)

The allylboronate ester condenses very readily with hexachlorocyclopentadiene forming the ester of 2-{1,4,5,6,7,7-hexachlorobicyclo[2,2,1]hept-5-en-1-yl]-methylboronic acid. The reaction of the allylboronate ester with 1,2,3,4-tetrachlorocyclopentadiene yields the ester of 2-{1,4,5,6-tetrachlorobicyclo[2,2,1]hept-5-en-1-yl}methylboronic acid.

Triallylborane, tricrotylborane, and tri-(2-methylallyl)borane react with ethyl diazoacetate, forming the esters of $\gamma\delta$-unsaturated acids (XVIII):[61]

$$(RCH{=}CR'CH_2)_3B + N_2CHOOC_2H_5 \xrightarrow[-N_2]{+H_2O} \underset{\text{(XVIII)}}{RCH{=}CR'(CH_2)_2COOC_2H_5};$$

R and R = H or CH_3.

According to some data[23], treatment of triallylborane with bromine at room temperature yields tri-(2,3-dibromopropyl)borane, while according to others[8] the product is 1,2,3-tribromopropane at –35°C. Reaction of di-n-butyl allylboronate with bromine yields the ester of 2,3-dibromopropylboronic acid[62]. In the presence of air, triallylborane forms a polymer containing 25–30% of oxygen[63]. Triallylborane is an active catalyst of the polymerisation of methyl methacrylate[63]. Thermal decomposition of triallylborane leads to the formation of various hydrocarbons and boron-containing products[64,65]. The reaction of triallylborane with tri-isobutylborane at 130–140°C yields butene and a polymer, which are converted on heating with alcohols into 1,5-dialkoxy-1,5-diboracyclo-octanes[66].

3. Reactions with Diborane and Tetra-alkyldiboranes

When triallylborane is treated with diborane (in proportions of 1 : 2) in ethereal solution, a solid polymer is obtained[67]. On being heated with n-butyl alcohol, it gives rise to hydrogen, propene, and liquid products, consisting mainly of 1,5-di-n-butoxy-1,5-diboracyclo-octane and the tetra-n-butyl ester of propane-1,3-diboronic acid. On heating with methyl borate, the solid polymer undergoes exchange reactions as a result of which the tetramethyl ester of propane-1,3-diboronic acid and the methyl ester of di-(3-dimethoxyborylpropyl)boronic acid are obtained[68–70]. When the polymer is heated with boron trichloride, 1,3-dichloroborylpropane is formed[71].

The reaction of triallylborane with triethylamine-borane leads to a polymer, whose pyrolysis gives rise to a complex mixture of products, where the main component is 1,5-diborabicyclo[3,3,3]undecane[72].

Hydroboration of dimethyl allylboronate and subsequent oxidation of the products lead to a mixture of diols containing 97% of propane-1,3-diol and 3% of propane-1,2-diol.[30] The main hydroboration product is tri-(3-dimethoxyborylpropyl)borane (XIX):

$$3\,CH_2{=}CHCH_2B(OCH_3)_2 + \frac{1}{2}B_2H_2 \rightarrow B[CH_2CH_2CH_2B(OCH_3)_2]_3.$$

(XIX)

On treatment with alcohol in the presence of a catalytic amount of a mercaptan, it is converted into the methyl ester of di-(3-dimethoxyborylpropyl)borinic acid and the dimethyl ester of n-propylboronic acid.

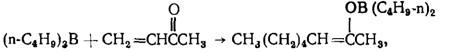
In the reaction of diborane with n-butyl diallylboronate, boron is attached to the extent of 97% to the terminal carbon atom of the allyl group[73]. The hydroboration of the ester with the reactants in proportions of 1 : 2 leads to a complex mixture of products whose treatment with n-butyl alcohol leads to the evolution of hydrogen and distillation of the alcoholysis products yields 1,5-di-n-butoxy-1,5-diboracyclo-octane and 1,3-dibutoxyborylpropane. The reaction of tetra-n-propyldiborane with dimethyl allylboronate results in the formation of the unstable dimethyl ester of 3-di-n-propylborylpropylboronic acid[74], which decomposes on heating into methyl di-n-propylboronate and a polymer. On heating with methyl borate in the presence of a small amount of tetrapropyldiborane, which plays the role of the reaction catalyst[75], the polymer is converted into 1,3-bis(dimethoxyboryl)propane. Allylboronate esters behave similarly in relation to tetra-alkylborane [...part of text missing in Russian original (Ed. of Translation)] dimethylester of allylthioboronic acid[74].

4. Reactions with Carbonyl Compounds and Nitriles

It has been reported[23,24] that triallylborane reacts with aldehydes to form the alkyl esters of diallylborinic acid and cyclohexadiene or dialkyl esters of alkylboronic acid, cyclohexadiene, and propene. Subsequently it was shown that the reaction of triallylborane with aldehydes in reality proceeds via the mechanism of organometallic synthesis, i.e. via the addition of allyl groups to the carbon atom and of the BR_2 group to the oxygen atom of the carbonyl group[76]. Depending on the ratio of the initial reactants, the esters of diallylborinic, allylboronic, or boric acids are then obtained. The reaction of triallylborane with ketones stops at the stage involving the formation of allylboronic acid even on heating to 80°C.[76]

Since allylboronate esters and borates are readily hydrolysed and readily undergo transesterification with aminoalcohols, the reaction of triallylborane with aldehydes and ketones can be used to synthesise unsaturated alcohols. The reaction of tricrotylborane with formaldehyde is accompanied by the allyl rearrangement[9]. Triallylborane adds smoothly to $\alpha\beta$-unsaturated aldehydes in the 1,2-positions[77,78]. The reaction of acrolein and triallylborane in 2 : 1 proportions yields the di(hexa-1,5-dien-3-yl)-ester of allylboronic acid[77,78]. The reaction of triallylborane with α-cyclocitral or β-cyclocitral (in proportions of 1 : 3) results in the formation of the corresponding borates, which demonstrates the ability of allylboronate esters to add to aldehydes.

The reactions of triallylborane with $\alpha\beta$-unsaturated ketones have also been investigated[77,79]. In contrast to tri-n-butylborane, which adds to methyl vinyl ketone in the 1,4-positions with formation of oct-2-en-2-yl dialkylborinate (XX):[77]



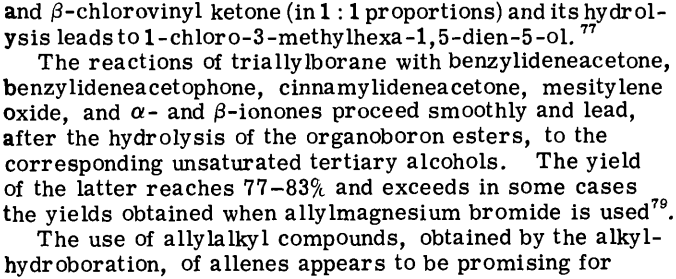
$$(n\text{-}C_4H_9)_3B + CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \rightarrow CH_3(CH_2)_4CH{=}\overset{\overset{\displaystyle OB(C_4H_9\text{-}n)_2}{|}}{C}CH_3,$$

(XX)

triallylborane adds to methyl vinyl ketone in the 1,2-positions with formation of the 3-methylhexa-1,5-dien-3-yl ester of diallylborinic acid, whose hydrolysis gives rise to 3-methylhexa-1,5-dien-3-ol. 1-Chloro-3-methylhexa-1,5-dien-3-yl diallylborinate is obtained from triallylborane and β-chlorovinyl ketone (in 1 : 1 proportions) and its hydrolysis leads to 1-chloro-3-methylhexa-1,5-dien-5-ol.[77]

The reactions of triallylborane with benzylideneacetone, benzylideneacetophone, cinnamylideneacetone, mesitylene oxide, and α- and β-ionones proceed smoothly and lead, after the hydrolysis of the organoboron esters, to the corresponding unsaturated tertiary alcohols. The yield of the latter reaches 77–83% and exceeds in some cases the yields obtained when allylmagnesium bromide is used[79].

The use of allylalkyl compounds, obtained by the alkylhydroboration, of allenes appears to be promising for organic synthesis. When these compounds interact with carbonyl derivatives, the products are the alkyl esters of dialkylborinic acids, whose hydrolysis yields unsaturated alcohols. Thus the esters (XXI) are formed from dialkyl-(3-methylbut-2-en-1-yl)boranes and mesityl oxide, their hydrolysis resulting in the formation of 3,3,4,6-tetramethylhepta-1,5-dien-4-ol (XXII):[17]



$$\begin{matrix}CH_3\\ & C{=}CHCH_2BR_2\\ CH_3\end{matrix} + (CH_3)_2C{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \xrightarrow[81\%]{} CH_2{=}CH{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OBR_2}{|}}{C}}{-}CH{=}C(CH_3)_2 \xrightarrow[86\%]{-H_2O}$$

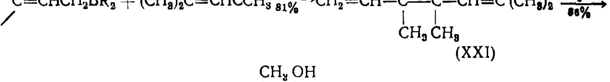
(XXI)

$$\rightarrow CH_2{=}CH{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}CH{=}C(CH_3)_2.$$

(XXII)

The reactions with acetone, methyl vinyl ketone, and benzaldehyde take place similarly.

Diallyl-(2-ethoxypenta-1,4-dien-1-yl)borane reacts with acetone to form compound (XXIII):[80]

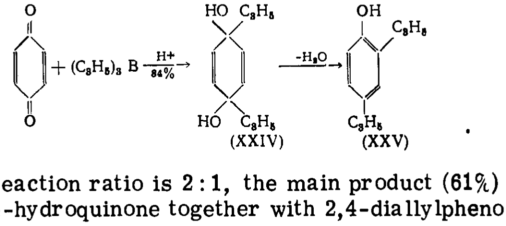


$$(C_3H_5)_2BCH{=}\overset{\overset{\displaystyle OC_2H_5}{|}}{C}{-}CH_2CH{=}CH_2 + 2(CH_3)_2CO \rightarrow CH_2{=}CHCH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}OBCH{=}\overset{\overset{\displaystyle OC_2H_5}{|}}{C}CH_2CH{=}CH_2.$$

(XXIII)

Di-n-hexyl crotylboronate reacts with butyraldehyde and cyclohexanone, the products being the corresponding 1-methylallylmethanols[27].

The reactions of triallylborane with various quinones have been investigated[81-83]. When triallylborane is allowed to react with 1,4-benzoquinone in 1 : 1 proportions and the resulting organoboron compounds are hydrolysed, the *cis*- and *trans*-isomers of 1,4-diallyl-1,5-dihydroxycyclohexa-2,5-diene (XXIV) are obtained in high yield and are converted on steam distillation in the presence of boric acid into 2,4-diallylphenol (XXV):

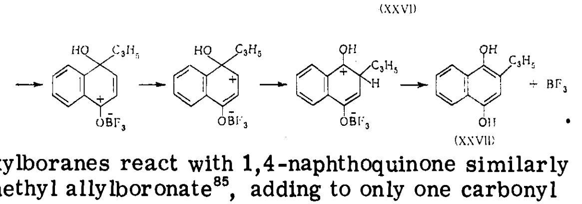


(XXIV) (XXV)

When the reaction ratio is 2 : 1, the main product (61%) is 2-allyl-1,4-hydroquinone together with 2,4-diallylphenol (26%).[83]

The reactions of triallylborane with substituted 1,4-benzoquinones have been investigated[82]. The interaction of equimolar amounts of 2-allyl-1,4-benzoquinone and triallylborane leads to the formation of 2,4,6-triallylphenol while the interaction of the reactants in proportions of 2 : 1 leads to the formation of insignificant amounts of 2,4,6-triallylphenol, the main reaction products being 2,5-diallyl- and 2,6-diallyl-1,4-hydroquinones. 2-Butyl-1,4-benzoquinone reacts with trialkylborane (in 1 : 1 proportions) with formation of 4,6-diallyl-2-butylphenol[83]. The reaction between 9,10-anthraquinone and triallylborane in equimolar proportions leads to 9-allyl-9-hydroxyanthrone and, when two equivalents of triallylborane are used, the main product is *cis*-9,10-diallyl-9,10-dihydroxy-9,10-dihydroanthracene with an admixture of the *trans*-isomer[83].

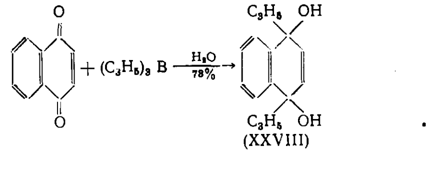
The esters of allylboronic and diallylborinic acids have proved to be extremely reactive in relation to quinones[82]. Dibutyl allylboronate gives a high yield of 2-allyl-1,4-hydroquinone on reaction with 1,4-benzoquinone. The mechanism of the formation of 2-allyl-1,4-hydroquinone was established in a study of the reaction between dimethyl allylboronate and 1,4-naphthoquinone. In this case it is possible to isolate the intermediate (when the reaction is carried out under mild conditions), namely 1-allyl-1-hydroxy-4-oxo-1,4-dihydronaphthalene (XXVI), which is converted into 2-allyl-1,4-dihydroxynaphthalene (XXVII) on heating with boron trifluoride-ether, as happens in the rearrangement of *p*-tolylquinol into 2-methyl-1,4-hydroquinone[84]:



(XXVI)

(XXVII)

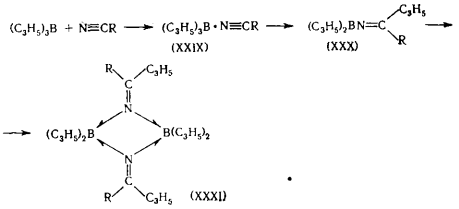
Trialkylboranes react with 1,4-naphthoquinone similarly to dimethyl allylboronate[85], adding to only one carbonyl group, while triallylborane adds readily to two carbonyl groups, forming, after hydrolysis, 1,4-diallyl-1,4-dihydroxy-1,4-dihydronaphthalene (XXVIII):[82]



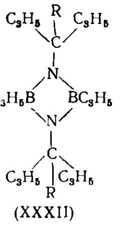
(XXVIII)

The reactions of triallylborane with 1,2-quinones have been investigated[83]. When equimolar amounts of 1,2-naphthoquinone and triallylborane interact, *trans*-1,2-diallyl-1,2-dihydroxy-1,2-dihydronaphthalene is formed after hydrolysis; the same diol is obtained also when 1,2-naphthoquinone is treated with dibutyl allylboronate. 9,10-Phenanthraquinone and acenaphthoquinone react similarly with triallylborane, forming respectively (after hydrolysis) 9,10-diallyl-9,10-dihydroxy-9,10-dihydrophenanthrene and 1,2-diallyl-1,2-dihydroxyacenaphthene (*trans*-configuration).

The first stage of the reaction of triallylborane with nitriles in isopentane between –70° and –50°C involves the formation of complexes (XXIX) which are completely converted, on gradual heating of the reaction mixture to room temperature, into substituted diallyl(but-3-enylidene-amino)boranes (XXX), which dimerise into derivatives of 2,2,4,4-tetra-allyl-1,3-di(but-3-enylidene)cyclodiborazane (XXXI):[86,87]



On heating (100°C), cyclodiborazanes are converted into substituted 2,4-diallyl-1,3-di(hepta-1,6-dien-4-yl)-1,3-diaza-2,4-diboretidines (XXXII), covalent B–N bonds being formed between boron and nitrogen atoms instead of the semicoordinate linkages B ← N, and N=C bonds being converted into single N–C linkages:



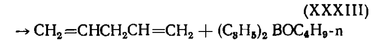
(XXXII)

Alcoholysis of diazadiboretidines yields 4-substituted 4-aminohepta-1,6-dienes.

5. Reactions with Compounds Containing an Activated Carbon–Carbon Double Bond

Allylboranes can react with compounds containing an activated double bond—vinyl ethers, 4,5-dihydro-2-methylfuran, and cyclopropene hydrocarbons.

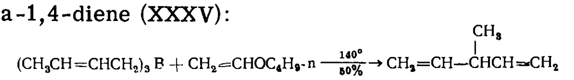
Triallylborane reacts with n-butyl vinyl ether at 110–140°C to form penta-1,4-diene (80% yield)[88,89]. Presumably allylborane initially adds to the double bond with formation of (2-alkoxypent-4-en-1-yl)diallylborane (XXXIII), which is then converted via β-elimination into the diene (XXXIV) and n-butyl diallylboronate:



$$(C_3H_5)_3B + CH_2{=}CHOC_4H_9\text{-}n \rightarrow \underset{\text{(XXXIII)}}{(C_3H_5)_2BCH_2{-}\overset{\overset{\displaystyle OC_4H_9\text{-}n}{|}}{C}HCH_2CH{=}CH_2} \rightarrow$$

$$\rightarrow \underset{\text{(XXXIV)}}{CH_2{=}CHCH_2CH{=}CH_2} + (C_3H_5)_2BOC_4H_9\text{-}n \quad .$$

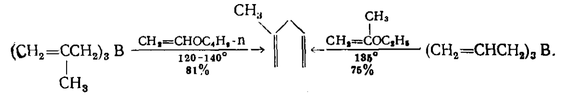
The ether (XXXIII) then reacts with a second molecule of vinyl ether via the same mechanism. The reaction of tricrotylborane with n-butyl vinyl ether yields 3-methylpenta-1,4-diene (XXXV):



$$(CH_3CH{=}CHCH_2)_3B + CH_2{=}CHOC_4H_9\text{-}n \xrightarrow[50\%]{140^\circ} \underset{\text{(XXXV)}}{CH_2{=}CH{-}\overset{\overset{\displaystyle CH_3}{|}}{C}HCH{=}CH_2} \quad .$$

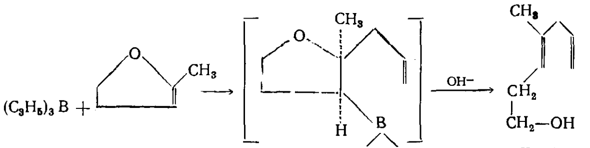
The formation of the diene (XXXV) shows that the addition of tricrotylborane to the carbon–carbon double bond proceeds with allyl rearrangement via a cyclic transition state.

2-Methylpenta-1,4-diene (XXXVI) is obtained from n-butyl vinyl ether and tri-(2-methylallyl)borane and also by the reaction of triallylborane with ethyl isopropenyl ether:



(XXXVI)

The reaction of triallylborane with 4,5-dihydro-2-methylfuran takes place slowly at room temperature and rapidly (in several minutes) at 80–100°C. Alkaline hydrolysis of the addition product leads to 4-methylhepta-1,4-dien-1-ol (XXXVII):

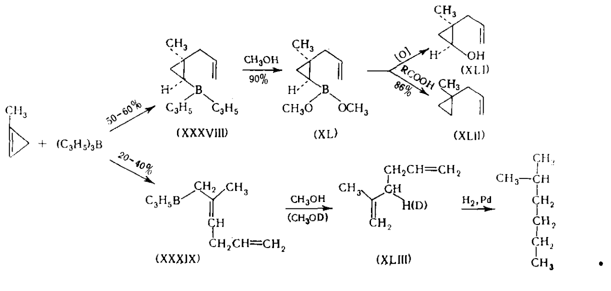


(XXXVII)

Thus reactions of allylboranes with acyclic and cyclic vinyl ethers constitute a convenient preparative method for the synthesis of 1,4-diene hydrocarbons and their derivatives with functional groups, which are otherwise difficult to obtain.

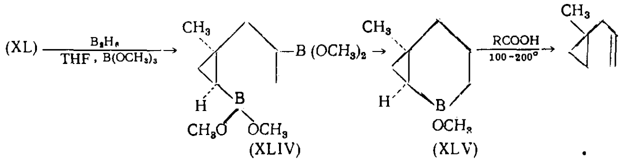
On cooling (to between –70° and 0°C), triallylborane reacts with 1-methylcyclopropene similarly to trialkylboranes[90], namely in two different ways. The preferred pathway involves the *cis*-addition of the organoborane to the double bond of the hydrocarbon with formation of diallyl-(1-allyl-1-methyl-2-cyclopropyl)borane (XXXVIII), but the reaction also takes place partly with rupture of the ring at the $C_{(2)}$–$C_{(3)}$ linkage with formation of diallyl-(2-methylhexa-2,5-dien-1-yl)borane (XXXIX). The methanolysis of compound (XXXVIII) gives rise to (1-allyl-1-methyl-2-cyclopropyl)dimethoxyborane (XL), the oxidation of which leads to 1-allyl-1-methyl-2-cyclopropanol (XLI) and acidolysis yields 1-allyl-1-methylcyclopropane (XLII).

Compound (XXXIX) has not been isolated in a pure state, but its formation has been demonstrated by the isolation of 2-methylhexa-1,5-diene (XLIII) from the products of the methanolysis of the reaction mass:

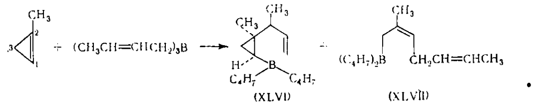


When 1-methyl-2-deuterocyclopropene is treated with triallylborane and the reaction products are subjected to methanolysis, 2-methyl-3-deuterohexa-1,5-diene (30–35%) and (1-allyl-2-deutero-1-methyl-2-cyclopropyl)dimethoxyborane (50–60%) are obtained.

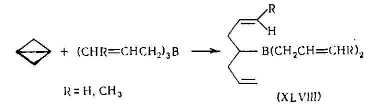
The hydroboration of compound (XL) in tetrahydrofuran (THF) in the presence of methyl borate leads to the diboron compound (XLIV), which is converted on heating (100–200°C) into 5-methoxy-5-methyl-5-borabicyclo[4,1,0]heptane [(5-methoxy-1-methyl-5-boranorcarane)] (XLV) with elimination of methyl borate[92]:



When 1-methylcyclopropene reacts with tricrotylborane, the main product (85–90%) is *cis*-[2-(but-3-en-2-yl)-2-methyl-1-cyclopropyl]di(but-2-enyl)borane (XLVI) together with di(but-2-enyl)-2-methylhepta-2,5-dien-1-ylborane (XLVII) (10–15%) yield); this shows that the addition of the allylborane to the double bond of the three-membered ring takes place with allyl rearrangement, while the insertion in a C–C single bond takes place without such rearrangement[93]:

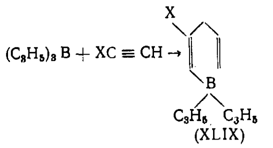


Triallylborane and tricrotylborane react at −70°C with bicyclo[1,1,0]butane to form the unsaturated compounds (XLVIII):[94]



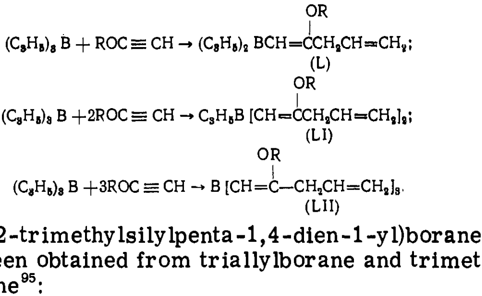
6. Reactions with Acetylenic Compounds

Acetylenic compounds react with triallylborane at room temperature to form 2-substituted diallyl-(2-penta-1,4-dien-1-yl)boranes (XLIX):



(2-Alkylpenta-1,4-dien-1-yl)diallylboranes (X = CH_3 or C_4H_9), obtained by the reaction of triallylborane with methylacetylene or n-butylacetylene[95-98], cannot be isolated in a pure state, since they are unstable and cyclise to 3-allyl-substituted 1,5-diallyl-1-boracyclohex-2-enes, the reaction being slow at room temperature and rapid on vacuum distillation[98].

2-Substituted diallyl(penta-1,4-dien-1-yl)boranes, formed in the first stage of the reaction of triallylborane with trimethylpropargyloxysilane[99], phenylacetylene[100], cyclohexenylacetylene[101], or propargyl chloride[102,103] are altogether unstable. However, alkoxyacetylenes react with triallylborane to form fairly stable addition products, which can be isolated in a pure state. The exothermic reaction of triallylborane with alkoxyacetylenes proceeds between −70° and −50°C and, depending on the reactant ratio, leads to (2-alkoxypenta-1,4-dien-1-yl)diallylboranes (L), di-(2-alkoxypenta-1,4-dien-1-yl)allylboranes (LI), or tri-(2-alkoxypenta-1,4-dien-1-yl)boranes (LII):[84,95]

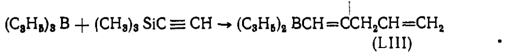


$$(C_3H_5)_3B + ROC \equiv CH \rightarrow (C_3H_5)_2BCH{=}\overset{\overset{\displaystyle OR}{|}}{C}CH_2CH{=}CH_2; \quad \text{(L)}$$

$$(C_3H_5)_3B + 2ROC \equiv CH \rightarrow C_3H_5B[CH{=}\overset{\overset{\displaystyle OR}{|}}{C}CH_2CH{=}CH_2]_2; \quad \text{(LI)}$$

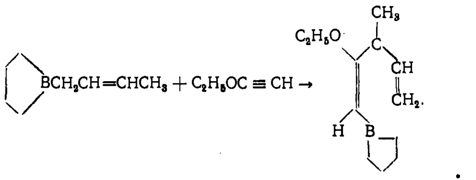
$$(C_3H_5)_3B + 3ROC \equiv CH \rightarrow B[CH{=}\overset{\overset{\displaystyle OR}{|}}{C}{-}CH_2CH{=}CH_2]_3. \quad \text{(LII)}$$

Diallyl-(2-trimethylsilylpenta-1,4-dien-1-yl)borane (LIII) has been obtained from triallylborane and trimethylsilylacetylene[95]:



$$(C_3H_5)_3B + (CH_3)_3SiC \equiv CH \rightarrow (C_3H_5)_2BCH{=}\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{C}CH_2CH{=}CH_2 \quad \text{(LIII)}$$

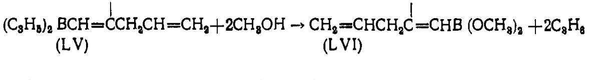
The first condensation stage, leading to compounds (XLIX), involves the *cis*-addition of $(C_3H_5)_2B$ and C_3H_5 fragments to the C≡C bond. The reaction probably proceeds via a six-centre transition state and is accompanied by the allyl rearrangement [as shown in a study of the reaction of 1-crotylboracyclopentane with ethoxyacetylene, which leads to the formation of 1-(2-ethoxy-3-methylpenta-1,4-dien-1-yl)boracyclopentane (LIV) [104,105]



(LIV)

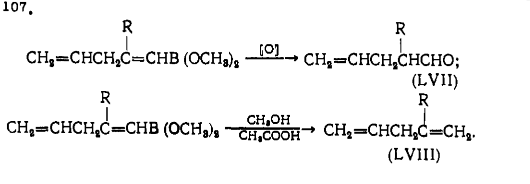
Tri-(2-methylallyl)borane reacts with alkoxyacetylenes like triallylborane. Depending on the reactant ratio, (2-alkoxy-4-methylpenta-1,4-dien-1-yl)di-(2-methylallyl)-boranes, di-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)-2-methylallylboranes, or tri-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)boranes are formed at temperatures between −70° and −20°C.[106]

On treatment with methanol, (2-alkylpenta-1,4-dien-1-yl)diallylboranes (LV) readily exchange their allyl groups for methoxy-groups[95-97,104]. The resulting dimethyl esters of 2-alkylpenta-1,4-dien-1-ylboronic acids (LVI),



$$\underset{\text{(LV)}}{(C_3H_5)_2BCH{=}\overset{\overset{\displaystyle R}{|}}{C}CH_2CH{=}CH_2} + 2CH_3OH \rightarrow \underset{\text{(LVI)}}{CH_2{=}CHCH_2\overset{\overset{\displaystyle R}{|}}{C}{=}CHB(OCH_3)_2} + 2C_3H_6$$

yield 2-alkylpent-4-enals (LVII) on oxidation with hydrogen peroxide and are converted into 2-alkylpenta-1,4-dienes (LVIII) on treatment with a mixture of methanol and acetic acid[96,97,107].

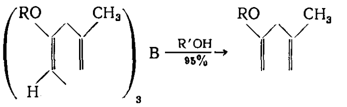


$$CH_2{=}CHCH_2\overset{\overset{\displaystyle R}{|}}{C}{=}CHB(OCH_3)_2 \xrightarrow{[O]} CH_2{=}CHCH_2\overset{\overset{\displaystyle R}{|}}{C}HCHO; \quad \text{(LVII)}$$

$$CH_2{=}CHCH_2\overset{\overset{\displaystyle R}{|}}{C}{=}CHB(OCH_3)_2 \xrightarrow[CH_3COOH]{CH_3OH} CH_2{=}CHCH_2\overset{\overset{\displaystyle R}{|}}{C}{=}CH_2. \quad \text{(LVIII)}$$

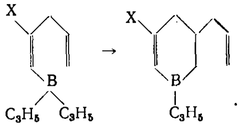
On treatment with alcohols, not only boron–allyl but also boron-vinyl bonds are ruptured in (2-alkoxypenta-1,4-dien-1-yl)diallylboranes and di-(2-alkoxypenta-1,4-dien-1-yl)allylboranes with formation, depending on the reactant ratio and the duration of heating, of 2-alkoxypenta-1,4-dienes or allyl methyl ketone ketals[104,107]. Tri-(2-alkoxypenta-1,4-dien-1-yl)boranes behave similarly with respect to alcohols.

Experiments on the alcoholysis of compounds (L)–(LII) by different alcohols have shown that the boron–vinyl bond dissociates via direct attack on the B–C linkage, which has been confirmed by studies on the reactions of tri-(2-methoxypenta-1,4-dien-1-yl)borane with methyl alcohol containing a labelled carbon atom[108]. The alcoholysis of tri-(2-alkoxy-4-methylpenta-1,4-dien-1-yl)-boranes (LIX) leads to 2-alkoxy-4-methylpenta-1,4-dienes (LX):[106]



(LIX) (LX) .

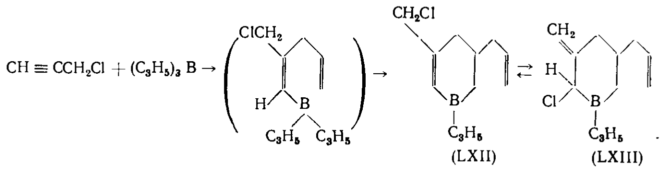
2-Substituted diallyl(penta-1,4-dien-1-yl)boranes (XLIX) can undergo intramolecular cyclisation to 3-substituted 1,5-diallyl-1-boracyclohex-2-enes (LXI):



(XLIX) (LXI) .

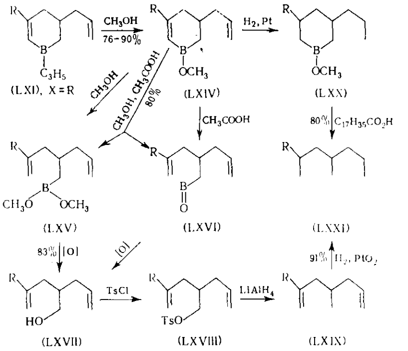
2-Alkyl-substituted compounds (XLIX, X = R) cyclise slowly at room temperature and rapidly on moderate heating (to 40–100°C).[96–98,109,110] 2-Alkoxy-substituted compounds (XLIX, X = OR) are converted into derivatives of type (LXI) at 120–130°C.[109,111] Compounds of type (LXI) are obtained by the reaction of triallylborane with trimethylpropargyloxysilane[99], phenylacetylene[100], and cyclohexylacetylene[101].

Propargyl chloride reacts slowly with triallylborane at room temperature, forming 1,5-diallyl-3-chloromethyl-1-boracyclohex-2-ene (LXII), which isomerises slowly to 1,5-diallyl-2-chloro-3-methylene-1-boracyclohexane (LXIII); after 20 days, the reaction mixture contains approximately 80% of compound (LXII) and 20% of compound (LXIII):[102,103]



(LXII) (LXIII) .

When 3-alkyl-1,5-diallyl-1-boracyclohex-2-enes (LXI) are treated with methanol at 20–30°C, propene is evolved and 3-alkyl-5-allyl-1-methoxy-1-boracyclohex-2-ene (LXIV) is formed[96,97,110]. When compound (LXIV) is refluxed for a long time with an excess of methanol, the B-vinyl bond is cleaved protolytically and (4-alkyl-2-allylpent-4-en-1-yl)dimethoxyborane (LXV) is formed. The ring opening in compound (LXIV) takes place much more rapidly when it is heated (to 80°C) with a mixture of methanol and acetic acid. Under these conditions, the products are the ester (LXV) and the trimer of the anhydride of (4-alkyl-2-allylpent-4-en-1-yl)boronic acid (LXVI) or the trimer (LXVI) alone when the reaction mixture is kept at room temperature for 24 h:



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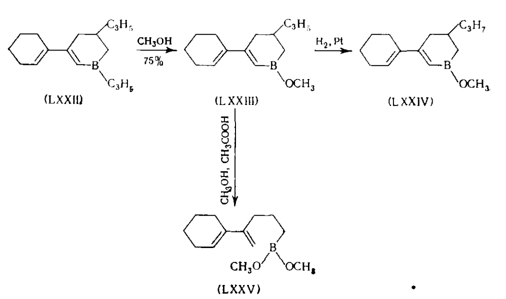
The oxidation of the esters (LXV) or the anhydrides (LXVI) with hydrogen peroxide in an alkaline medium gives an 80–90% yield of 4-alkyl-2-allylpent-4-en-1-ols (LXVII). By reducing the tosylates (LXVIII) with lithium aluminium hydride, it is possible to obtain 2,4-dimethylhepta-1,6-diene (LXIX, R = CH_3) or 2-n-butyl-4-methylhepta-1,6-diene (LXIX, R = n-C_4H_9). Hydrogenation of the methoxy-derivatives (LXIV) over platinum black leads to 3-alkyl-1-methoxy-5-n-propyl-1-boracyclohexenes (LXX). 1-Methoxy-3-methyl-5-n-propyl-1-boracyclohexane can be converted by acidolysis into 2,4-dimethylheptane (LXXI, R = CH_3). 5-Allyl-1-methoxy-3-phenyl-1-boracyclohex-2-ene, obtained by the methanolysis of 1,5-diallyl-3-phenyl-1-boracyclohex-2-ene, is hydrogenated in steps to 1-methoxy-3-phenyl-5-n-propyl-1-boracyclohex-2-ene (over platinum black) and 1-methoxy-3-phenyl-5-n-propyl-1-boracyclohexane (over $Pd/SrCO_3$).[100]

On treatment with methanol, 1,5-diallyl-3-cyclohexenyl-1-boracyclohex-2-ene (LXXII) is converted into 5-allyl-3-cyclohexenyl-1-methoxy-1-boracyclohex-2-ene (LXXIII), which gives rise to 3-cyclohexenyl-1-methoxy-5-n-propyl-1-boracyclohex-2-ene (LXXIV) on hydrogenation over Pt black and (2-allyl-4-cyclohexenylpent-4-en-1-yl)-dimethoxyborane (LXXV) on treatment with a mixture of methanol and acetic acid[101]:



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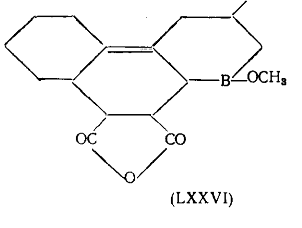
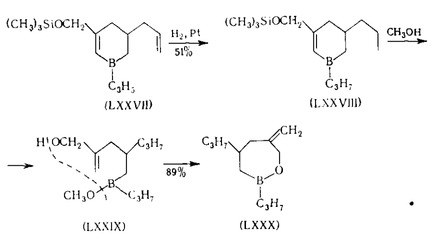
Compound (LXXIV) undergoes the diene condensation with maleic anhydride, forming the anhydride of 3-allyl-1-methoxy-1-boradodecahydrophenanthrenedicarboxylic acid (LXXVI):



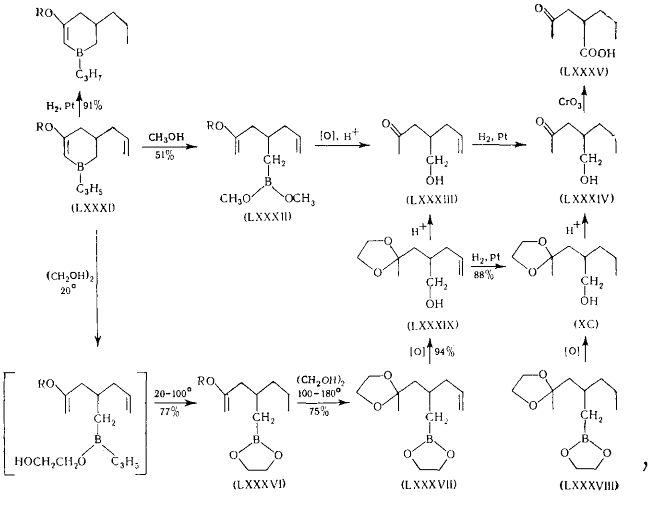
(LXXVI) .

1,5-Diallyl-3-trimethylsiloxymethyl-1-boracyclohex-2-ene (LXXVII) is hydrogenated over the Adams catalyst to 1,5-di-n-propyl-3-trimethylsiloxymethyl-1-boracyclohex-2-ene (LXXVIII), which is smoothly converted on brief heating with methanol [with cleavage of the Si–O– and B–C= bonds and subsequent intramolecular condensation of compound (LXXIX)] into 6-methylene-2,4-di-n-propyl-1-2-oxaborepan (LXXX):[99]



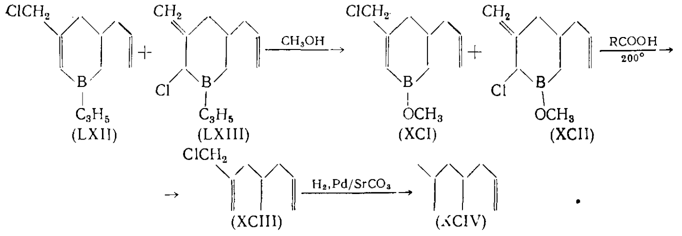
2,4-Dimethylheptane can be obtained from compound (LXXX) by a series of consecutive operations.

On treatment with alcohols, the boron–vinyl ring bond is initially broken in 3-alkoxy-1,5-diallyl-1-boracyclohex-2-ene (LXXXI), as shown by infrared spectroscopy, and the boron–allyl bond then undergoes alcoholysis in the resulting acyclic organoboron complex[111]. The final product of the reaction of compound (LXXXI) with methanol is (4-alkoxy-2-allylpent-4-en-1-yl)dimethoxyborane (LXXXII), from which it is possible to obtain 4-hydroxymethylhept-1-en-6-one (LXXXIII), 4-hydroxymethylheptan-6-one (LXXXIV), and 2-n-propyl-levulinic acid (LXXXV). When compound (LXXXI) is heated with ethylene glycol, the resulting product is 2-(4-alkoxy-2-allylpent-4-en-1-yl)-1,3,2-dioxaborolan (LXXXVI), which yields 2-(2-allyl-4,4-ethylenedioxy-1-pentyl)-1,3,2-dioxaborolan (LXXXVII) on further heating (100–180°C) with ethylene glycol. Catalytic hydrogenation and oxidation with hydrogen peroxide of the last product results in its conversion into 2-(4,4-ethylenedioxy-2-n-propyl-1-pentyl)-1,3,2-dioxaborolan (LXXXVIII), 2-allyl-4,4-ethylenedioxy-pentanol (LXXXIX), and 4,4-ethylenedioxy-2-n-propyl-1-pentanol (XC), from which it is possible to obtain compounds (LXXXIII)–(LXXXV):

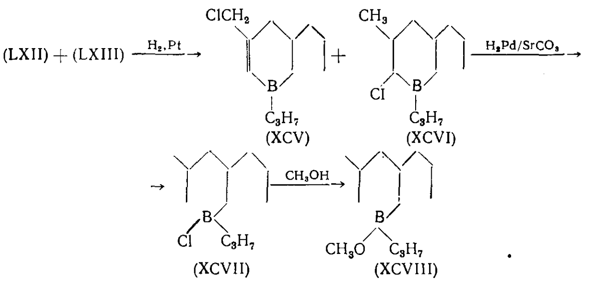


where R = CH_3 or n-C_4H_9.

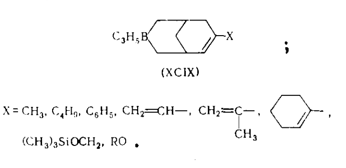
Methanolysis of a mixture of 1,5-diallyl-3-chloromethyl-1-boracyclohex-2-ene (LXII) and 1,5-diallyl-2-chloro-3-methylene-1-boracyclohexane (LXIII) in proportions of 4 : 1 results in a mixture of 5-allyl-3-chloromethyl-1-methoxy-1-boracyclohex-2-ene (XCI) and 5-allyl-1-methoxy-3-methylene-1-boracyclohexane (XCII), which are converted by acidolysis into 2-chloromethyl-4-methylhepta-1,6-diene (XCIII). The last compound is hydrogenated over Pd/$SrCO_3$ to 2,4-dimethylheptane (XCIV):[101]



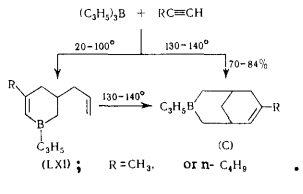
Hydrogenation of a mixture of compounds (LXII) and (LXIII) over platinum yields 3-chloromethyl-1,5-di-n-propyl-1-boracyclohex-2-ene (XCV) and 2-chloro-3-methyl-1-di-n-propyl-1-boracyclohexane (XCVI). On further hydrogenation over Pd/$SrCO_3$, compounds (XCV) and (XCVI) are converted into chloro-n-propyl-(4-methyl-2-n-propyl-1-pentyl)borane (XCVII), which is converted on treatment with methanol into the methyl ester of (4-methyl-2-n-propyl-1-pentyl)-n-propylboronic acid (XCVIII). Acidolysis of the chloride (XCVII) yields 2,4-dimethylheptane (XCIV):



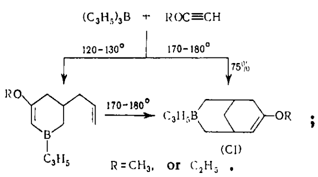
3-Substituted 1,5-diallyl-1-boracyclohex-2-enes (LXI) undergo intramolecular cyclisation on heating (130–180°C) with formation of 7-substituted 3-allyl-3-borabicyclo[3,3,1]non-6-enes (XCIX):



The reaction of triallylborane with acetylene (at 120–130°C) yields directly 3-allyl-3-borabicyclo[3,3,1]non-6-ene (XCIX, X = H).[112,113] The synthesis of 7-alkyl-3-allyl-3-borabicyclo[3,3,1]non-7-enes (C) requires a temperature of 130–140°C:[113,114]

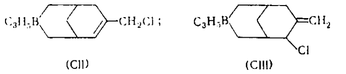


In order to obtain 7-alkoxy-3-allyl-3-borabicyclo[3,3,1]non-6-enes (CI), the reaction must be carried out at 170–180°C:[115]



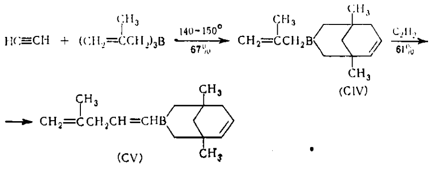
3-Allyl-7-trimethylsiloxymethyl-3-borabicyclo[3,3,1]non-6-ene is formed in 80% yield when triallylborane is heated with trimethylpropargyloxysilane at 140°C;[116] in order to synthesise 3-allyl-7-phenyl-3-borabicyclo[3,3,1]non-6-ene (in 96% yield), a mixture of triallylborane and phenylacetylene is kept for 1 h at 80°C:[100] 3-allyl-7-cyclohexenyl-3-borabicyclo[3,3,1]non-6-ene is formed when 1,5-diallyl-3-cyclohexenyl-1-boracyclohex-1-ene is vacuum-distilled[117].

When propargyl chloride is heated with triallylborane, a mixture of 3-allyl-7-chloromethyl-3-borabicyclo[3,3,1]non-6-ene (CII) and 3-allyl-6-chloro-7-methylene-3-borabicyclo[3,3,1]nonane (CIII) is formed in proportions of 7 : 3:[102,118]



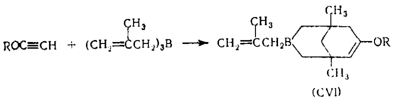
When triallylborane and propargyl bromide are heated, they form a mixture of 3-allyl-7-bromomethyl-3-borabicyclo[3,3,1]non-6-ene and 3-allyl-6-bromo-7-methylene-3-borabicyclo[3,3,1]nonane[119].

When tri-(2-methylallyl)borane is heated in acetylene in an autoclave at 140–150°C, 1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CIV) is formed in 67% yield; it can add to acetylene with formation of compound (CV):[120,121]

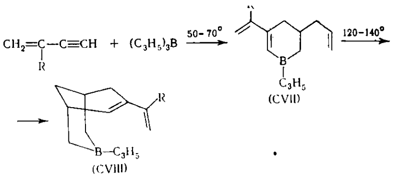


Tri-(2-methylallyl)borane reacts with n-butylacetylene to form 7-n-butyl-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene[120].

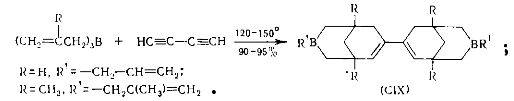
7-Alkoxy-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-enes (CVI) have been obtained by the condensation of tri-(2-methylallyl)borane with alkoxyacetylenes[120,122]:



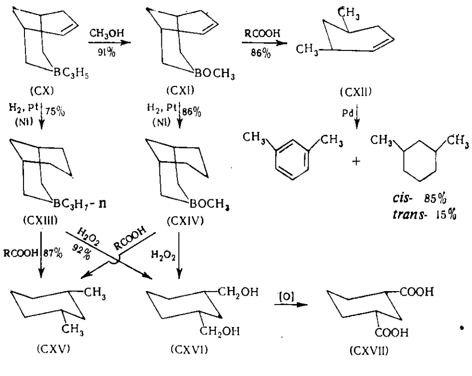
The interaction of triallylborane with vinylacetylene or isopropenylacetylene results in the formation of 1,5-diallyl-3-vinyl-1-boracyclohex-2-ene (CVII, R = H) or 1,5-diallyl-3-isopropenyl-1-boracyclohex-2-ene (CVII, R = CH_3) respectively, which are converted on heating into 3-allyl-7-vinyl-3-borabicyclo[3,3,1]non-6-ene (CVIII, R = H) or 3-allyl-7-isopropenyl-3-borabicyclo[3,3,1]non-6-ene (CVIII, R = CH_3):[123-125]



The reaction of diacetylene with triallylborane or tri-(2-methylallyl)borane at 120–150°C leads to the dibora-compounds (CIX) with a system of conjugated double bonds[126]:

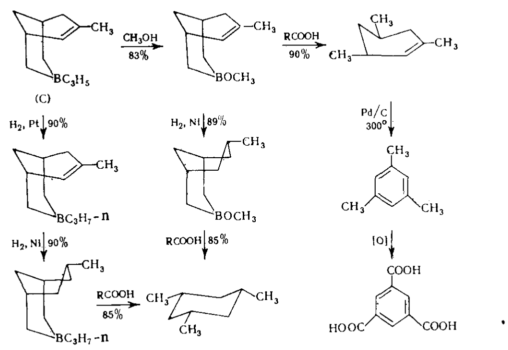


The methanolysis of 3-allyl-3-borabicyclo[3,3,1]non-6-ene (CX) leads to 3-methoxy-3-borabicyclo[3,3,1]non-6-ene (CXI),[113] which is converted into *cis*-3,5-dimethylcyclohexene (CXII) on heating with caproic acid as a result of the cleavage of the B–C bonds. When the THF solution of compound (CXII) is heated with palladium black, a mixture of *m*-xylene and *cis*- and *trans*-1,3-dimethylcyclohexanes is formed. The double bonds in the bicyclic compounds (CX) and (CXI) are readily hydrogenated at 20°C over a platinum catalyst at atmospheric pressure or over Raney nickel in an autoclave, the products being 3-n-propyl-3-borabicyclo[3,3,1]nonane (CXIII) or 3-methoxy-3-borabicyclo[3,3,1]nonane (CXIV) respectively, probably having the chair–chair conformation like bicyclo[3,3,1]nonane. The acidolysis of compounds (CXIII) and (CXIV) leads to *cis*-1,3-dimethylcyclohexane (CXV) with only about 1% of unidentified impurities. The oxidation of compounds (CXIII) and (CXIV) with hydrogen peroxide in an alkaline medium results in the formation of *cis*-1,3-dihydroxymethylcyclohexane (CXVI), which is converted on further oxidation into *cis*-cyclohexane-1,3-dicarboxylic acid (CXVII):



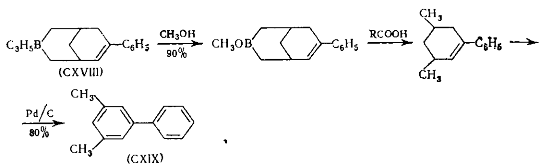
When compound (CX) is heated with n-butylamine, it is converted into 3-n-butylamino-3-borabicyclo[3,3,1]non-6-ene which can be obtained also by the transamination of 3-amino-3-borabicyclo[3,3,1]non-6-ene. The last compound can be obtained by the action of ammonia on 3-n-butylthio-3-borabicyclo[3,3,1]non-6-ene, formed by the reaction of thioborate and 3-methoxy-3-borabicyclo[3,3,1]non-6-ene[127]. The synthesis of 3-alkylthio- and 3-amino-3-borabicyclo[3,3,1]nonanes has been achieved similarly[127].

3-Allyl-7-methyl-3-borabicyclo[3,3,1]non-6-ene (C, R =CH_3) has been subjected to the following reactions[112]:

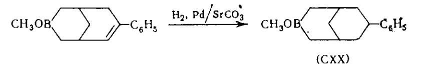


Similar reactions have been achieved with 3-allyl-7-n-butyl-3-borabicyclo[3,3,1]non-6-ene[114].

The structure of 3-allyl-7-phenyl-3-borabicyclo-[3,3,1]non-6-ene (CXVIII) has been demonstrated by converting it into 3,5-dimethylbiphenyl (CXIX):[100]

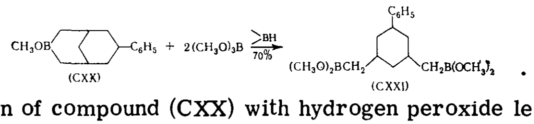


In contrast to 3-methoxy-7-methyl-3-borabicyclo-[3,3,1]non-6-ene, compound (CXVIII) is not hydrogenated in an autoclave over Raney nickel but it can be readily hydrogenated with hydrogen in 7-methoxy-7-phenyl-3-bora-bicyclo[3,3,1]nonane (CXX) in the presence of Pd/$SrCO_3$ at room temperature[100]:

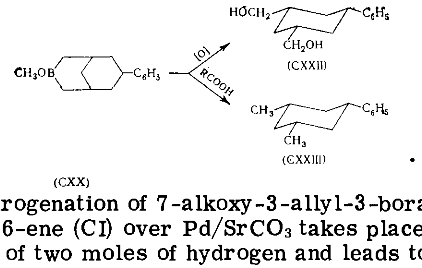


(CXX)

When compound (CXX) is heated with methylborate for a long time in the presence of tetra-n-propyldiborane, the boron-containing ring is cleaved and 1,3-bis(dimethoxy-borylmethyl)-5-phenylcyclohexane (CXXI) is formed:

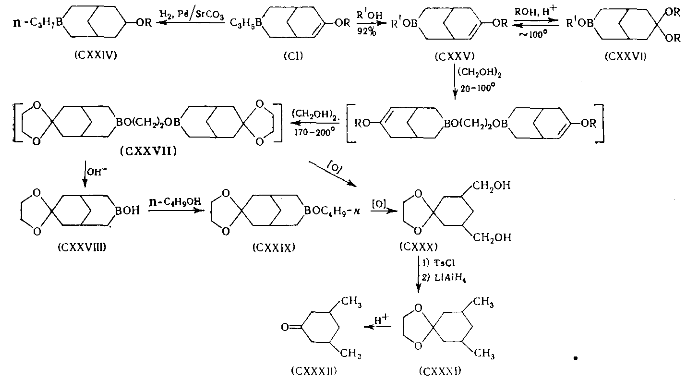


Oxidation of compound (CXX) with hydrogen peroxide leads to the synthesis of 1,3-dihydroxymethyl-5-phenylcyclo-hexane (CXXII) and, when the latter is heated with stearic acid, it is possible to obtain *cis*-1,3-dimethyl-5-phenyl-cyclohexane (CXXIII):

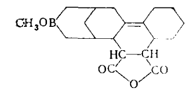


(CXX)

The hydrogenation of 7-alkoxy-3-allyl-3-borabicyclo-[3,3,1]non-6-ene (CI) over Pd/$SrCO_3$ takes place with absorption of two moles of hydrogen and leads to 7-alkoxy-3-n-propyl-3-borabicyclo[3,3,1]nonane (CXXIV).[115] The dialkoxy-derivatives (CXXV) are formed with liberation of propene when compounds (CI) are treated with alcohols. In the presence of acids, the alkoxy-derivative (CXXV), containing the vinyl ether group, readily combines with alcohols to form ketals (CXXVI), which are, however, unstable and split off the alcohol on vacuum distillation (at about 100°C) with reformation of the initial bicyclic compound. Cyclic diboraketals (CXXVII) can be obtained by heating the bicyclic compounds (CI) or (CXXV) with ethylene glycol. The bicyclic acid (CXXVIII) can be obtained by the alkaline hydrolysis of the ethylene ketal (CXXVII) and can be converted by esterification with n-butyl alcohol into 3-n-butoxy-7,7-ethylenedioxy-3-bora-bicyclo[3,3,1]nonane (CXXIX). The oxidation of the cyclic ketal (CXXIX) or the diketal (CXXVII) with hydrogen peroxide in an alkaline medium led to 1,1-ethylenedioxy-*cis*-3,5-dihydroxymethylcyclohexane (CXXX), the reduction of the di-*p*-tosylate of which with lithium aluminium hydride led to the synthesis of 1,1-ethylenedioxy-*cis*-3,5-dimethylcyclohexane (CXXXI). Under the influence of dilute acid, the last compound was converted into *cis*-3,5-dimethylcyclohexanone (CXXXII):

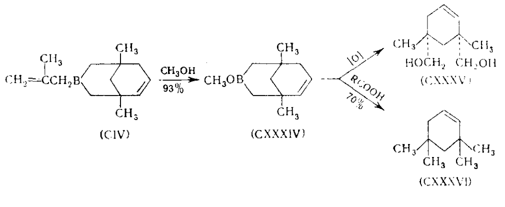


7-Cyclohexenyl-3-methoxy-3-borabicyclo[3,3,1]non-6-ene undergoes the diene condensation with maleic anhydride, forming compound (CXXXIII):[117]

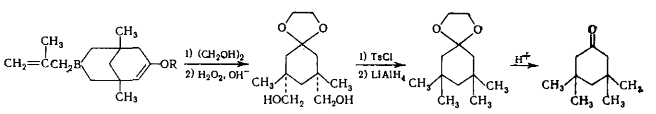


(CXXXIII)

The methanolysis of 1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CIV) leads to 3-methoxy-1,5-dimethyl-3-borabicyclo[3,3,1]non-6-ene (CXXXIV), the oxidation of which with hydrogen peroxide affords *cis*-3,5-di(hydroxymethyl)-3,5-dimethylcyclohex-1-ene (CXXXV) and its acidolysis gives rise to 3,3,5,5-tetra-methylcyclohexene (CXXVI):[120]

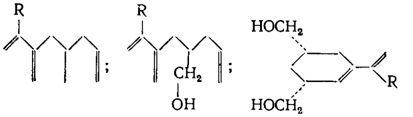


On treatment with ethylene glycol followed by oxidation with hydrogen peroxide in an alkaline medium, 7-alkoxy-1,5-dimethyl-3-(2-methylallyl)-3-borabicyclo[3,3,1]non-6-ene (CVI) can be converted into 1,1-ethylenedioxy-*cis*-3,5-di(hydroxymethyl)-1,3-dimethylcyclohexane (CXXXVII), the reduction of the tosylate of which with lithium aluminium hydride yields 1,1-ethylenedioxy-3,3,5,5-tetramethylcyclohexane (CXXXVIII). The hydrolysis of the last compound results in the formation of 3,3,5,5-tetramethylcyclohexanone (CXXXIX):[120]



(CVI) (CXXXVII) (CXXXVIII) (CXXXIX)

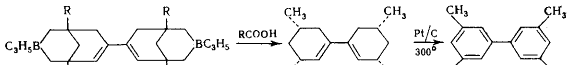
Compounds (CVII) are converted by acidolysis or combined acidolysis and oxidation into the triene hydrocarbons (CXL) or the triene alcohols (CXLI). Oxidation of compounds (CVIII) yields *cis*-di(hydroxymethyl)vinylcyclohexenes (CXLII):[123–125]



(CXL) (CXLI) (CXLII)

R=H,CH_3

Compound (CXLIII) and 3,3′,5′,5′-tetramethylbiphenyl (CXLIV) can be obtained from compound (CIX, R = H) by a series of consecutive chemical reactions[126]:



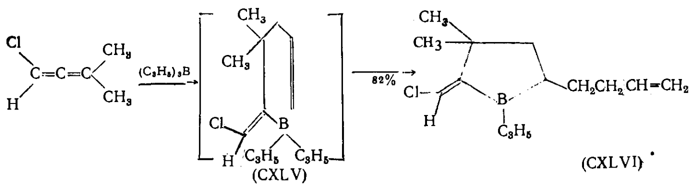
(CIX), R=H (CXLIII) (CXLIV)

Thus a stereospecific method for the synthesis of cyclohexene and cyclohexane derivatives has been developed on the basis of the allylborane–acetylene condensation.

7. Reactions with Allenes

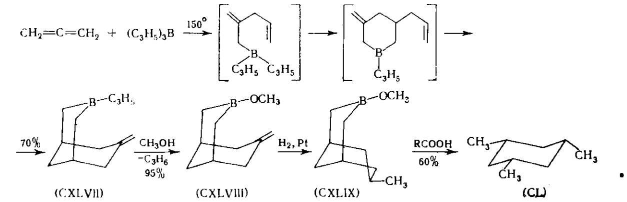
Like acetylenes, allenes can react with allylboranes, forming cyclic compounds, the ease of the reactions and their direction depending on the nature of the allene component.

The reactions of allylboranes with 1-chloro-3-methylbuta-1,2-diene, allene, and 3-methylbuta-1,2-diene have been investigated. It has been found that 1-chloro-3-methylbuta-1,2-diene reacts slowly with triallylborane even at room temperature, forming 1-allyl-2-(but-3-en-1-yl)-5-chloromethylene-4,4-dimethylboracyclopentane (CXLVI).[128,129] By analogy with the allylborane–acetylene condensation, the first reaction stage evidently consists of the addition of triallylborane to the allene system, the diallylboryl group adding to the central carbon atom and the allyl group to the terminal carbon atom joined to two methyl groups. The resulting diallyl-(1-chloromethylene-2,2-dimethylpent-4-en-1-yl)borane (CXLV) undergoes intramolecular cyclisation at room temperature, but the mode of cyclisation is in this case different from that of the pentadienyl derivatives of boron of type (LXIX), i.e. the allyl group adds to the terminal carbon atom of the pentene system and the boron atom adds to a non-terminal atom:



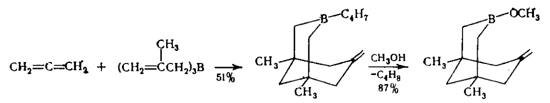
(CXLV) (CXLVI)

Allene, which has less polarised bonds, is more inert with respect to allylboranes than 1-chloro-3-methylbuta-1,2-diene. It reacts slowly with triallylborane on heating (at 150°C) in an autoclave, giving a 60% yield of 3-allyl-7-methylene-3-borabicyclo[3,3,1]nonane (CXLVII), the structure of which has been established by infrared spectroscopy and NMR and also by conversion into known compounds[129–131]. On treatment with methanol, compound (CXLVII) is smoothly converted into 3-methoxy-7-methylene-3-borabicyclo[3,3,1]nonane (CXLVIII), the catalytic hydrogenation of which yields 3-methoxy-7-methyl-3-borabicyclo[3,3,1]nonane (CXLIX). The last compound, which had been obtained previously from methylacetylene and triallylborane[113], is converted on acidolysis into the known *cis*-1,3,5-trimethylcyclohexane (CL):



(CXLVII) (CXLVIII) (CXLIX) (CL)

The reaction of allene with tri-(2-methylallyl)borane proceeds similarly but under more severe conditions[129,131]. When an equimolar mixture of the reactants is heated in an autoclave at 160–170°C, the product is 1,5-dimethyl-7-methylene-3-(2-methylprop-2-en-1-yl)-3-borabicyclo-[3,3,1]nonane (CLI):

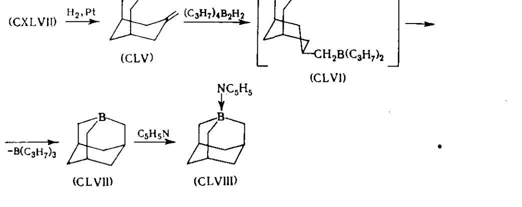


(CLI) (CLII)

8. The Synthesis of 1-Bora-adamantane Derivatives

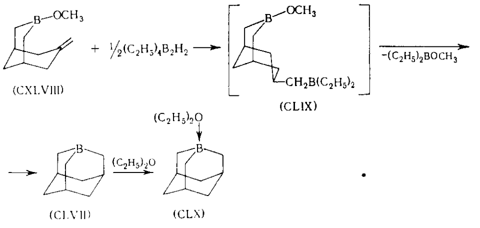
Derivatives of 3-borabicyclo[3,3,1]nonane with a methylene group in the 7-position, obtained by the condensation of allylboranes with allenes, have been used to synthesise 1-bora-adamantanes. Different versions of this synthesis are based on the hydroboration of the 7-methylene group and subsequent intramolecular cyclisation of the resulting dibora-compounds, which had been found previously in a series of acyclic dibora-[132,133],and tri-bora-systems[70].

In the first version, 3-allyl-7-methylene-3-borabicyclo-[3,3,1]nonane (CXLVII) was partly hydrogenated with hydrogen over platinum black to give 7-methylene-3-n-propyl-3-borabicyclo[3,3,1]nonane (CLV), which was then hydroborated by tetra-n-propyldiborane to 3-n-propyl-7-di-n-propylborylmethyl-3-borabicyclo[3,3,1]nonane (CLVI), the latter cyclising to 1-boratricyclo[3,3,1,$1^{3,7}$]-decane (1-bora-adamantane) (CLVII) with elimination of 3-n-propylborane. The bora-adamantane forms a stable adduct [CLVIII] with pyridine[129,131,134,135]:



(CLV) (CLVI) (CLVII) (CLVIII)

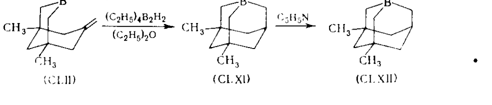
1-Bora-adamantane can be obtained more conveniently by the hydroboration of 3-methoxy-7-methylene-3-borabicyclo[3,3,1]nonane (CXLVIII), since the latter compounds can be synthesised more simply than compound (CLV). Diborane in an ethereal medium or a tetra-alkyldiborane may be used as the hydroborating agent. When compound (CXLVIII) is treated with tetraethyldiborane, the product is 7-diethylborylethyl-3-methoxy-3-borabicyclo[3,3,1]nonane (CLIX), which is converted with elimination of methyl diethylborinate into 1-bora-adamantane and the latter can be isolated by distillation or in the form of the ether adduct (CLX) or the pyridine adduct (CLVIII):



In the hydroboration of compound (CXLVIII) with diborane in an ethereal medium, the ether adduct (CLX) formed can be isolated (after the vacuum distillation of the solvent and methyl borate, which is also produced in the reaction) in the form of a colourless viscous liquid. If compound (CXLVIII) is hydroborated with diborane in THF solution, the product is the tetrahydrofuran complex of 1-bora-adamantane in 72% yield.

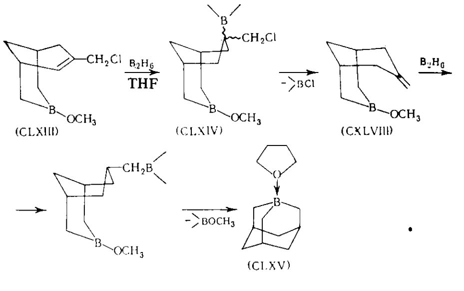
The ether complex of 1-bora-adamantane is comparatively stable, but it partly dissociates into the components even at room temperature. The ether adduct (CLX) has been used to synthesise complexes with other ligands having a more marked electron-donating capacity by simple mixing of the reactants in an inert solvent[129,135]. The thermally stable complex of 1-bora-adamantane with THF and very stable complexes with pyridine and triethylamine, which do not dissociate even at 200°C, have been obtained in this way. A complex of 1-bora-adamantane with ethyl acetate has been synthesised by the interaction of these reactants.

3-Methoxy-1,5-dimethyl-7-methylene-3-borabicyclo-[3,3,1]nonane (CLII) is smoothly converted on treatment with tetraethyldiborane in an ethereal medium into the ether adduct of 3,5-dimethyl-1-bora-adamantane (CLXI). Treatment of compound (CLXI) with pyridine yields the pyridine adduct (CLXII):[129,131]

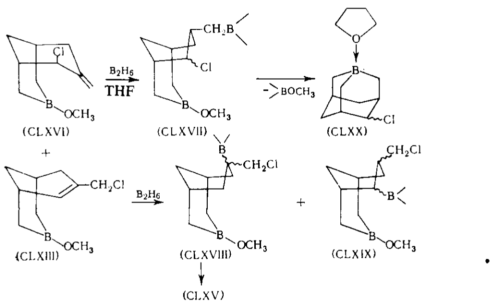


The method of synthesis of the 1-bora-adamantane system described here has been used to obtain 1-bora-adamantane derivatives with functional groups from compounds formed in the allylborane–acetylene condensation.

On treatment with diborane in THF, 7-chloromethyl-3-methoxy-3-borabicyclo[3,3,1]non-6-ene (CLXIII) combines with boron to the extent of 27% in the β-position relative to the CH_2Cl group, forming the borane (CLXIV). The latter eliminates compound (CXLVIII), which is converted as a result of hydroboration and cyclisation into the tetrahydrofuran complex of 1-bora-adamantane (CLXV):[136]



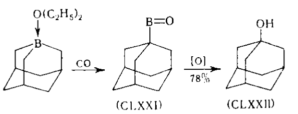
When a 4:1 mixture of compound (CLXIII) and 6-chloro-3-methoxy-7-methylene-3-borabicyclo[3,3,1]nonane (CLXVI) is treated with a tetra-alkyldiborane, a mixture of boranes (CLXVII)–(CLXIX) is formed. The borane (CLXVII) cyclises to 4-chloro-1-bora-adamantane, which can be isolated from the reaction mixture as the adduct (CLXX) with THF. The borane (CLXVIII) is converted by a series of stages into the tetrahydrofuran complex of 1-bora-adamantane (CLXV), which can be isolated from the reaction mixture by vacuum distillation[136]:



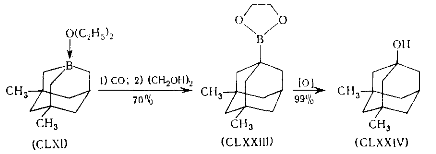
1-Bora-adamantane is a unique compound in which the boron atom is in a tetrahedral state and not in a trigonal valence state as in all the tervalent boron compounds known hitherto. This feature of 1-bora-adamantane is reflected in its chemical properties, in particular in its enhanced tendency towards complex formation. 1-Bora-adamantane forms very stable coordination compounds with pyridine and trimethylamine, which do not dissociate even at 200°C. It also forms complexes with ethyl ether and ethyl acetate, a ^{11}B NMR study of the stability of which made it possible to estimate experimentally the energy of the rearrangement of trialkylborane in its transition during complex formation from the planar to the pyramidal configuration; it proved to be 6–10 kcal mole^{-1}.[129]

9. Synthesis of Adamantanes

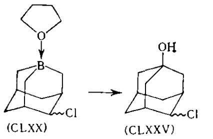
Hillman's studies[137-139] have shown that trialkylboranes are converted into trialkylmethanols on treatment with carbon monoxide and subsequent oxidation of the carbonylation products, 1-Bora-adamantanes undergo similar reactions. The ether adduct of 1-bora-adamantane reacts at room temperature with carbon monoxide, forming the anhydride of 1-adamantylboronic acid (CLXXI). The oxidation of the anhydride of the acid or its ester by an alkaline solution of hydrogen peroxide leads to 1-hydroxyadamantane (CLXXII):[129,131]



The carbonylation of the ether adduct (CLXI) to the anhydride of 3,5-dimethyl-1-adamantylboronic acid proceeds just as smoothly; the oxidation of its ethylene glycol ester (CLXXIII) gives an almost quantitative yield of 1-hydroxy-3,5-dimethyladamantane (CLXXIV):[129,131]



The tetrahydrofuran complex of 4-chloroboraadamantane (CLXX) is converted by carbonylation with carbon monoxide into 4-chloro-1-hydroxyadamantane (CLXXV):[136]



The study of the reactions of allylboranes with acetylenes and allenes has led to the discovery of new methods of synthesising adamantane derivatives, which may be of practical value, since many compounds of the adamantane series possess physiological activity. Compounds with antiviral, antitumour[140], soporific[141], antimalarial[142], insecticidal[143], antidiabetic[144], antibacterial[145], neurotropic[146], curaremimetic[147,148], and other activities have been found in this series.

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New Data on Reactions of Organofluorine Compounds

I.L.Knunyants and V.R.Polishchuk

The review surveys data obtained in recent years for chemical reactions of organofluorine compounds. Data for new reactions of these compounds are considered in combination with new concepts concerning the mechanisms of processes known previously separated ionic and radical reactions.
The bibliography includes 280 references.

CONTENTS

Methods for the introduction of fluorine into organic molecules as well as data obtained by physical methods for organofluorine compounds have been considered in an earlier review[1]. The present review surveys the available information about their chemical reactions.

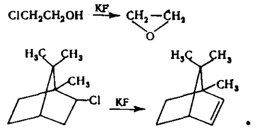
I. ANIONOID REACTIONS

Reactions of this type are most common in the chemistry of organofluorine compounds. A number of reviews have been devoted to their detailed discussion[2-6].

1. Fluorocarbanions Generated with the Aid of Fluoride Ions

The fluoride ion plays an exceptionally important role in the chemistry of organofluorine compounds. Historically the first compound containing the C–F bond (benzoyl fluoride) was obtained by Borodin in 1862 by treating benzoyl chloride with potassium hydrogen fluoride[7].

The high basicity of potassium fluoride, which was already known to Berzelius (quoted after Borodin[7]), began to be used from 1947, when the dehydrochlorination of β-chloroethanol and bornyl chloride was achieved[8]:



Subsequent studies showed that anhydrous salts of hydrofluoric acid are very strong bases. Thus tetraethylammonium fluoride splits off HCl from β-phenylethyl chloride 800 times faster than sodium ethoxide[9]. Strong CH acids (nitro-compounds with pK_a < 7) form salts upon reaction with alkali metal fluorides in an alcoholic medium[10]. On the other hand, in an aprotic medium, the anion is generated even from a CH acid with pK_a = 25 (acetonitrile[11]). Triphenylmethane (pK_a = 28.8) virtually does not form an anion[12].

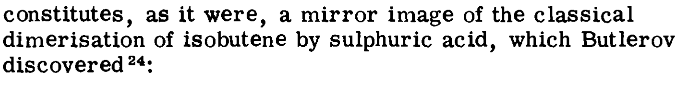
The extremely high energy of the hydrogen bonds formed by the fluoride ion is the cause of certain experimental difficulties associated with the use of thermally unstable tetra-alkylammonium fluorides, from which it is impossible to eliminate completely the water of crystallisation (two H_2O molecules remain[12,13]).

The highest degree of charge delocalisation is acheved when F^- is incorporated in an octahedral cage containing 4 or 6 water molecules. The hydration energies calculated by the CNDO method (128 and 117 kcal mole^{-1} respectively) agree well with the experimental value of 120 kcal mole^{-1}.[14] The high energy of the H–F hydrogen bond is also the cause of acid catalysis in the hydrolysis of, for example, benzyl fluoride[15] (the mechanisms of fluorine-substitution reactions have been reviewed[16]). In the absence of solvation (in the gas phase), the nucleophilic properties of F^- (determined from the kinetics of its reaction with CH_3Cl) are close to those of OH^- and NH_2^- (determined mass-spectrometrically[17]).

Alkali metal fluorides form compounds with hydrogen peroxide[18] just as readily as with water and, like alkalis, with carbon dioxide[19] ($F_2CO_2^{2-}$ is analogous to CO_3^{2-}) and isocyanates[20]:

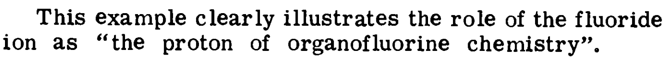
$$FSO_2NCO + MF \rightarrow FSO_2\bar{N}CO F\overset{+}{M};$$
$$M = Na,\ K,\ Cs.$$

The ability of the fluoride ion to add to the electrophilic double bonds of fluorine-containing olefins[21] and carbonyl compounds[22] is extremely important for organofluorine chemistry. The anions formed are capable of a series of transformations analogous to those of carbonium ions in the chemistry of hydrocarbons. Thus the dimerisation of octafluoroisobutene under the influence of caesium fluoride[23],



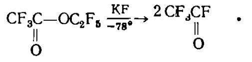
$$(CF_3)_2C{=}CF_2 \xrightarrow[(C_2H_5)_2O]{CsF} [(CF_3)_3\bar{C}] \xrightarrow{(CF_3)_2C=CF_2} \rightarrow (CF_3)_3C{-}CF{=}C(CF_3)_2 + (CF_3)_3C{-}CF_2{-}\underset{\displaystyle CF_3}{\underset{|}{C}}{=}CF_2\ ,$$

constitutes, as it were, a mirror image of the classical dimerisation of isobutene by sulphuric acid, which Butlerov discovered[24]:



$$(CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} [(CH_3)_3\overset{+}{C}] \xrightarrow{(CH_3)_2C=CH_2} \rightarrow (CH_3)_3C{-}CH{=}C(CH_3)_2 + (CH_3)_3C{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2\ .$$

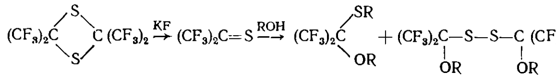
This example clearly illustrates the role of the fluoride ion as "the proton of organofluorine chemistry". Oligomerisation catalysed by the fluoride ion is also characteristic of other polyfluorinated olefins or carbonyl compounds. It has been shown for hexafluoropropene that this reaction is reversible (when the trimer C_3F_6 is heated with CsF, it is partly converted into the dimer and the monomer[25]). The reversibility of the dimerisation of trifluoroacetyl fluoride is much more marked: in the presence of KF, its dimer ("perfluoroethyl perfluoroacetate") decomposes at −78°C [26]:



$$CF_3C(=O){-}OC_2F_5 \xrightarrow[-78°]{KF} 2\,CF_3CF{=}O \quad .$$

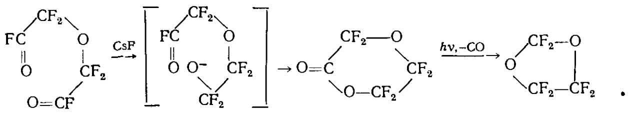
In the absence of fluorine atoms in the *gem*-position relative to the oxygen atom, fully fluorinated esters, for example dodecafluoro-t-butyl acetate, are resistant to the action of CsF even on heating[27].

The dimers of fully fluorinated thioketones also dissociate in the presence of fluoride ions, which makes it possible to generate their monomeric form directly in the reaction medium[28]:

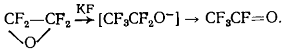


R=CH_3, C_2H_5, C_3H_7.

In contrast to fluoro-olefins, the oligomerisation of which usually stops at the stage involving the formation of trimers or tetramers, hexafluorobut-2-yne forms a polymer on treatment with KF under analogous conditions[29]. An elegant application of "internal dimerisation" in combination with ultraviolet irradiation made it possible to synthesise hexafluoro-1,3-dioxacylopentane[30]:

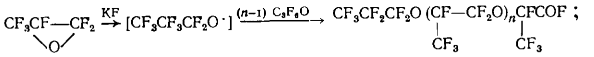


Not only carbonyl compounds, but also fluoro-oxirans, which rearrange under the influence of the fluoride ion into acyl fluorides, can serve as sources of "perfluoroalkoxides" [31]:



$$\underset{\diagdown O \diagup}{CF_2{-}CF_2} \xrightarrow{KF} [CF_3CF_2O^-] \rightarrow CF_3CF{=}O.$$

The method of synthesising hexafluoromethyloxiran is based on this reaction:

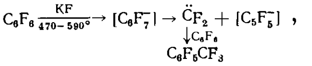


$$\underset{\diagdown O \diagup}{CF_3CF{-}CF_2} \xrightarrow{KF} [CF_3CF_3CF_2O^\cdot] \xrightarrow{(n-1)\ C_3F_6O} CF_3CF_2CF_2O\,(\underset{CF_3}{CF}{-}CF_2O)_n\underset{CF_3}{CF}COF\ ;$$

n=0—35.

Oligomers in which the terminal acyl fluoride group is replaced by another more inert group are used as lubricating materials and hydraulic liquids[32].

Unusual reactions occur when hexafluorobenzene is treated with potassium fluoride under severe conditions. Together with the formation of fully fluorinated toluene and xylenes, which evidently occurs with participation of difluorocarbene[33],



$$C_6F_6 \xrightarrow[470-590°]{KF} [C_6F_7^-] \rightarrow \underset{\substack{\downarrow C_6F_6 \\ C_6F_5CF_3}}{\ddot{C}F_2} + [C_5F_5^-]\ ,$$

decafluoromethylcyclopentene is also formed in this reaction[34].

The oligomerisation of a fluoro-olefin or a carbonyl compound can be suppressed when the anion is generated in the presence of electrophilic agents capable of reacting with it†. Thus, when octafluoroisobutene is treated with caesium fluoride in the presence of CH_3I, alkylation and not the dimerisation of the olefin takes place[35]:

$$(CF_3)_2C{=}CF_2 + CsF + CH_3I \rightarrow (CF_3)_3C{-}CH_3.$$

In the presence of acrylic acid derivatives, products resulting from the formal addition of $(CF_3)_3CH$ to them are formed after treatment with water[35]:

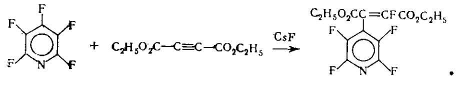
$$(CF_3)_2C{=}CF_2 \xrightarrow{CsF} [(CF_3)_3\overline{C}] \xrightarrow{CH_2=CHX}$$

$$\rightarrow [(CF_3)_3C{-}CH_2{-}\overline{C}HX] \xrightarrow{H_2O} (CF_3)_3C{-}CH_2{-}CH_2{-}CH_2X;$$

$$X{=}CN,\ COOCH_3.$$

The nonafluoro-t-butyl anion substitutes halogen atoms just as readily in unsaturated and aromatic compounds—pentafluoropyridine, cyanuryl chloride, 1-fluoro-2,4-dinitrobenzene, *p*-fluoronitrobenzene [36], and chlorophenylacetylene.[37] From the standpoint of synthetic possibilities in the series of aromatic fluoro-compounds such as octafluorotoluene, pentafluoropyridine, and others, this reaction may be compared with Friedel-Crafts alkylation. The carbanions generated from hexafluoropropene, tetrafluoroethylene, and other fluoro-olefins can also be involved in this reaction[4,5,38].

An anion capable of similar reactions is generated as a result of the addition of F^- to the electrophilic triple bond of the acetylene dicarboxylate ester [39]:



The reaction involving hexafluorobut-2-yne is complicated by polymerisation.

The fluorinated carbanions are capable of adding to cationoid species, forming stable covalent compounds. It has been possible to synthesise in this way mixed azo-compounds[40]:

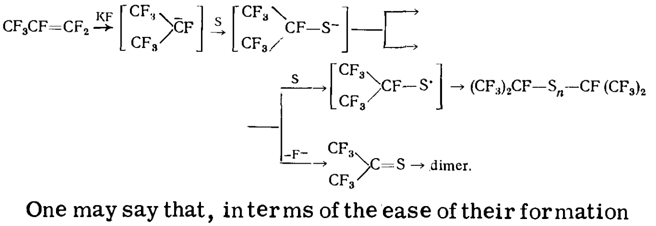
$$R_f^- + C_6H_5N_2^+Cl^- \rightarrow R_fN{=}NC_6H_5;$$

or metal fluoroalkyl derivatives[41-43]:

$$R_f^- + M^+ \rightarrow R_f - M;$$

$$M{=}Ag,\ {}^1/_2\,Hg \quad .$$

When fluorocarbanions are treated with elemental sulphur, the products are mercaptide anions capable of both eliminating the fluoride ion (which leads to thiocarbonyl compounds) and of being oxidised by the excess sulphur with formation of di- and poly-sulphides[44]:



One may say that, in terms of the ease of their formation and the scope of their synthetic applications, "perfluorocarbanions" (actually ionised fluoroalkyl derivatives of alkali metals) can replace to some extent Grignard reagents in fluorine chemistry. In view of the instability of Grignard reagents associated with the ease of elimination of magnesium fluoride, evidently only those fluorine-containing Grignard reagents which contain unsaturated or primary fluoroalkyl residues can be of some preparative value[45].

The attempts at direct detection of fluorocarbanions with with the aid of ^{19}F NMR showed that these species are in a state of rapid exchange. Thus the exchange between the nonafluoro-t-butyl anion and octafluoroisobutene in

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†See the review of B. L. Dyatkin (deceased), N. I. Delyagina, and S. R. Sterlin "The Perfluoro-t-butyl Anion in the Synthesis of Organofluorine Compounds" in this issue.

1,2-dimethoxyethane cannot be made slow in terms of the NMR time scale even at −100°C [46]:

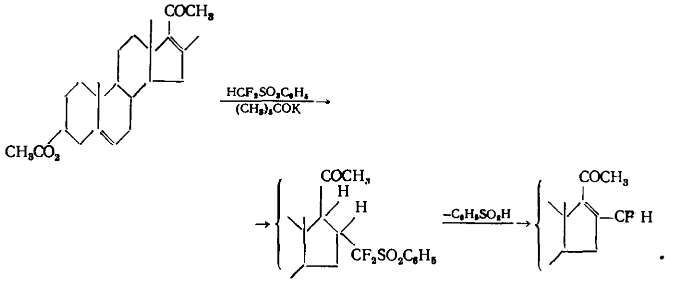
$$(CF_3)_2\bar{C}{-}CF_2{-}F + CF_2{=}C(CF_3)_2 \rightleftharpoons (CF_3)_2C{=}CF_2 + CF_3{-}\bar{C}(CF_3)_2 \,.$$

Comparison of fluoro-olefins and carbonyl compounds in their reactions with the fluoride ion showed that the latter are more reactive: trifluoroacetyl fluoride exchanges with $Cs^{18}F$ seven times faster than hexafluoropropene [47]. Hexafluoroacetone, taken in a minimal excess, causes the complete dissolution of ceasium fluoride in acetonitrile, while one of the most electrophilic fluoro-olefins (octafluoroisobutene) causes only a slight increase of the solubility of CsF in aprotic solvents. By virtue of this feature, hexafluoroacetone is used for the preparation of extremely reactive highly dispersed CsF (by the vacuum evaporation of a solution of "perfluoroalkoxide" [48]).

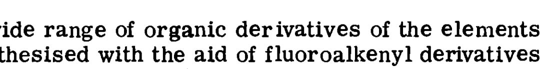
2. Fluorocarbanions Generated by Other Methods

Apart from the methods specific to fluorocarbanions—the addition of the fluoride ion to electrophilic multiple bonds—they can be generated by the general methods of carbanion chemistry. As a result of the high proton mobility of the hydrogen atom at a tertiary carbon atom in polyfluoroalkanes, fluorocarbanions are generated when the alkanes are treated with comparatively weak bases. Thus the reaction of the nonafluoro-t-butylanion with acrylic systems, discussed above, can be achieved also by treating acrylic systems with a mixture of $(CF_3)_3CH$ and triethylamine [49]. Kinetically independent carbanions can probably be in fact involved in processes of this kind. The study of the kinetics of the dehydrohalogenation of compounds having the general formula $C_6H_6CHClCF_3X$, where X = F or Cl, showed that the presence of a chlorine atom in the β-position greatly accelerates the process, probably in consequence of synchronous elimination. If, on the other hand, X = F, a kinetically independent carbanion is evidently formed [50].

Base-catalysed reactions, which ultimately reduce to the insertion of a carbene, can also include a stage involving the formation of a carbanion [51]:



The hydrogen atom at the double bond of a fluoro-olefin can also be sufficiently acidic for the generation of perfluoroalkenyl anions [52]:



$$CF_2{=}CFH \xrightarrow[-100^\circ]{C_4H_9Li} CF_2{=}CFLi \xrightarrow{1)\,(CH_3)_2C{=}O;\ 2)\,H_2O} CF_2{=}CF{-}C(CH_3)_2{-}OH \,.$$

A wide range of organic derivatives of the elements can be synthesised with the aid of fluoroalkenyl derivatives of lithium or magnesium (see the review by Knuyants et al. [53]):

$$CF_2{=}CFMgBr + ECl_3 \rightarrow CF_2{=}CFECl_2;$$
$$E{=}P,\ As,\ Sb,\ Bi \,.$$

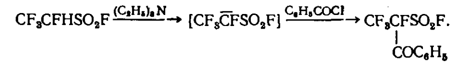
Trifluorovinyl derivatives of sulphur, silicon, germanium, tin, mercury, platinum, and palladium have been obtained similarly.

CH acids are also widely used for synthesising organomercury compounds—the sources of halogenocarbenes. For example [54]:

$$C_6H_5HgCl + CF_3CHFBr \xrightarrow[-35^\circ]{CH_3ONa} C_6H_5HgCFBrCF_3 \,.$$

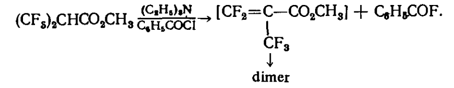
When the product is heated, trifluoromethylfluorocarbene is formed.

The anion generated when 1,2,2,2-tetrafluoroethanesulphonyl fluoride is treated with triethylamine can substitute the chlorine in benzoyl chloride [55]:



$$CF_3CFHSO_2F \xrightarrow{(C_2H_5)_3N} [CF_3\bar{C}FSO_2F] \xrightarrow{C_6H_5COCl} CF_3CF(COC_6H_5)SO_2F.$$

The analogous acylation of polyfluoro-α-hydrocarboxylic acids cannot be achieved; the main reaction pathway involved dehydrofluorination [56]:

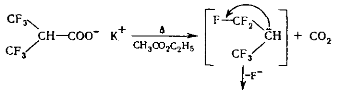


$$(CF_3)_2CHCO_2CH_3 \xrightarrow[C_6H_5COCl]{(C_2H_5)_3N} [CF_2{=}C(CF_3){-}CO_2CH_3] + C_6H_5COF.$$
$$[CF_2{=}C(CF_3){-}CO_2CH_3] \downarrow \text{dimer}$$

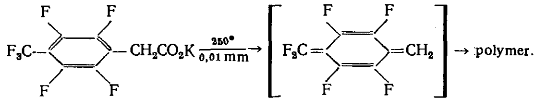
Benzoyl chloride has an electrophilic cooperative effect on dehydrofluorination, making it irreversible in consequence of the binding of the fluoride ion in the form of a covalent compound—benzoyl fluoride. Lewis acids, introduced in the form of complexes with tertiary amines, have a similar effect. The use of these complexes makes it possible to synthesise many interesting unsaturated compounds in preparative yields, for example [57]:

$$(CF_3)_2C{=}CF_2 + CH_2(CO_2C_2H_5)_2 \xrightarrow[-HF]{(C_2H_5)_3N\cdot BF_3} (CF_3)_2C{=}CFCH(CO_2C_2H_5)_2 \xrightarrow[-HF]{(C_2H_5)_3N\cdot BF_3}$$
$$\rightarrow (CF_3)_2C{=}C{=}C(CO_2C_2H_5)_2.$$

The leaving group in the generation of fluorocarbanions may be not only a proton but also CO_2, which makes it possible to use fluorocarboxylate salts in reactions of this kind. Decarboxylation can be used for the synthesis of fluoro-olefins [58]:



The synthesis of fluorine-containing quinonemethides, which form polymers on vacuum condensation on a cold surface, is carried out similarly [59]:



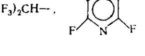
The elimination of CO_2 by fluorocarboxylate salts can be reversible (fluorocarbanions are capable of combining with carbon dioxide [60]). A method for the synthesis of nonafluoro-β-phenoxypropionic acid is based on this fact [61]:

$$C_6F_5OK + C_2F_4 \rightarrow [C_6F_5OCF_2\bar{C}F_2]\,K^+ \xrightarrow{CO_2} C_6F_5OCF_2CF_2COOK.$$

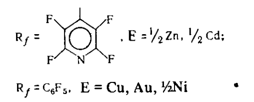
The decarboxylation of heavy metal salts has been used successfully in the synthesis of a wide variety of fluorine-containing organometallic compounds. The mechanism of this process may be more complex, involving a radical generation stage [62–66]:

$$R_f{-}CO_2{-}E \longrightarrow R_f{-}E + CO_2;$$

$R_f = (CF_3)_2CH{-}$,

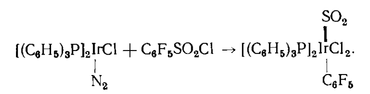


$E = \tfrac{1}{2}\,Hg;$



$R_f = C_6F_5$, E = Cu, Au, ½Ni

SO_2 or SO_3 can also be the leaving groups in reactions of this kind—for example in the synthesis of polyfluoroaryl derivatives of mercury[67],[68] or iron[69]. In the synthesis of σ-pentafluorophenyliridium, SO_2 is combined as the ligand, displacing molecular nitrogen[70]:



$$[(C_6H_5)_3P]_2\underset{\underset{N_2}{|}}{IrCl} + C_6F_5SO_2Cl \rightarrow [(C_6H_5)_3P]_2\overset{\overset{SO_2}{|}}{\underset{\underset{C_6F_5}{|}}{IrCl_2}}.$$

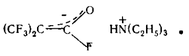
The decarboxylation of silver hexafluoroisobutyrate leads to the formation of hexafluoroisopropylsilver[71]:

$$(CF_3)_2CH—CO_2—Ag \rightarrow (CF_3)_2CH—Ag + CO_2.$$

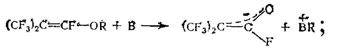
The basicity of the solvent has a significant influence on the ease of reaction: CO_2 is not evolved in boiling tetrahydrofuran (THF); in acetonitrile, the reaction takes place at 40–50°C and, in pyridine, at room temperature. This demonstrates the important role played in such reactions by the nucleophilic cooperation of solvent molecules. Such cooperation affects just as strongly the reactions of fluoroalkyl derivatives of heavy metals, which can be particularly readily coordinated to bases by virtue of the electron-accepting properties of the fluoroalkyl groups and can also serve as sources of fluorocarbanions. Thus the decomposition of bis(nonafluoro-t-butyl)mercury, which takes place readily in the presence of iodide salts in aprotic solvents, leads to the formation of octafluoroisobutene. The action of KF does not lead to the decomposition of the organomercury compound, but in the presence of KF it reacts much more readily with agents such as sulphur or iodine[72]:

$$[(CF_3)_3C]_2Hg \overset{F^-}{\rightleftarrows} [(CF_3)_3C]_2\overline{H}gF \xrightarrow{I_2} (CF_3)_3CI.$$

On treatment with triethylamine, hexafluoroisobutyryl fluoride (in contrast to the chloride) does not eliminate the hydrogen halide. The reaction stops at the stage involving the formation of a solid salt-like complex containing a mesomerically stabilised carbanion [73] (see the review of Knunyants et al.[74]):

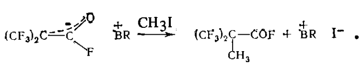


The extremely high stability of such fluorocarbanions makes it possible to obtain them by a novel method—by treating with bases alkyl polyfluorovinyl ethers, which have been found to be capable of acting as alkylating agents[75-77]:

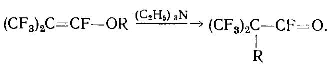
 (1)

R = CH_3, C_2H_5; B = $(C_2H_5)_3N$, $[(CH_3)_2N]_3PO$, C_5H_5N.

In its turn, the mesomeric anion can be also alkylated—for example with methyl iodide[78]:

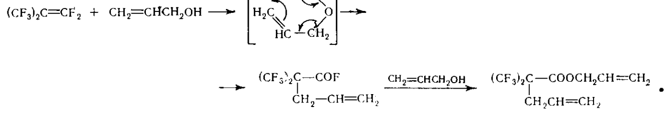


An excess of the initial vinyl ether can also serve as an alkylating agent, so that its heat treatment in the presence of bases leads to a rearrangement[79]:

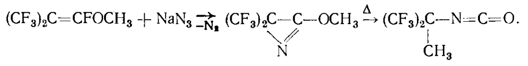


$$(CF_3)_2C=CF—OR \xrightarrow{(C_2H_5)_3N} (CF_3)_2\underset{\underset{R}{|}}{C}—CF=O.$$

The allyl group as the substituent R migrates particularly readily. For this reason, allyl heptafluoroisobutenyl ether cannot be synthesised at all: under the conditions of the reaction of octafluoroisobutene with an alcohol usually employed for this purpose, a rearrangement takes place immediately, so that the final product is allyl α-allylhexafluoroisobutyrate[80]:



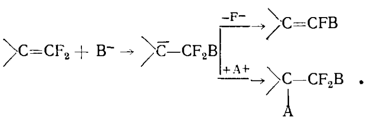
Evidently yet another rearrangement is of a related type—the conversion of 2,2-bis(trifluoromethyl)-3-methoxyazirine, obtained by treating heptafluoroisobutenyl methyl ether with sodium azide, into the corresponding isocyanate[81]:



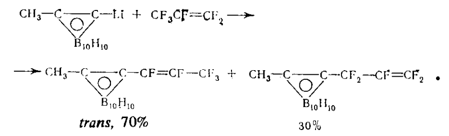
3. Reactions of Fluorine-Containing Unsaturated Compounds with Nucleophilic Agents

It has been shown[82] that the fluorine atom in the vinyl position of a fluoro-olefin is more mobile than the atom in the allyl position. This property is specific to organofluorine compounds and distinguishes them from the majority of substances for which the traditional concept of a greater mobility of the halogen atom in the allyl position is valid.

When a fluoro-olefin is attacked by an anion B^-, the intermediate carbanion may be stabilised either by eliminating the fluoride ion (substitution) or by combining with a cation A^+ (addition):

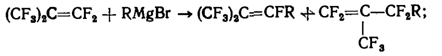
 (2)

When a fluoro-olefin is attacked by an uncharged nucleophilic species B′ with a lone electron pair, the product is a dipolar species $\rangle\bar{C}-CF_2-\overset{+}{B}'$, which can be stabilised not only by the two pathways indicated above, but also by a third pathway, leading to the formation of cycloaddition products. Studies in recent years make it possible to refine somewhat this general mechanism. Substitution in fluoro-olefins, initially studied in relation to nucleophilic agents ultimately forming in this reaction a substituent with a lone electron pair (HNR_2, RO^-) [82], can be directed to some extent also to the allyl position, provided that it results in the introduction of an electron-accepting substituent[83]:



However, the *meta*-carborane analogue, which has a smaller *–I* effect, forms exclusively the vinyl isomer[84].

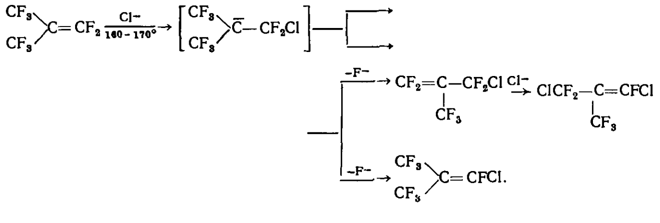
The interaction of octafluoroisobutene with Grignard reagents also leads to the partial formation of allyl isomers. The ratio of the reaction products depends on the nature of the group introduced[85]:



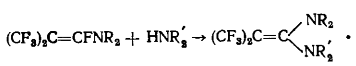
$$(CF_3)_2C{=}CF_2 + RMgBr \rightarrow \underset{(I)}{(CF_3)_2C{=}CFR} + \underset{(II)}{CF_2{=}\underset{\underset{CF_3}{|}}{C}{-}CF_2R};$$

$R{=}(CH_3)_2CH$, (I) : (II)=68 : 32; $R{=}n\text{-}C_4H_9$, (I) : (II) =82 : 18; $R{=}C_6H_5CH_2$, (I): (II)=60:40.

The reaction of octafluoroisobutene with the chloride ion occurring in the presence of phosphoryl chloride, which binds F^-, leads to a mixture of compounds which includes products of both vinyl and allyl substitution[86]:



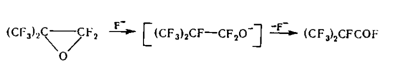
Fluoro-olefins with a non-terminal double bond were previously regarded as relatively unreactive. However, it has been shown recently that they are capable of reversible isomerisation to olefins with a terminal C=C bond on treatment with an attacking nucleophilic agent. As a result of this, it has been possible to introduce into the reaction with amines hexafluoropropene dimers, which constitute a mixture of $(CF_3)_2CFCF{=}CFCF_3$ and $(CF_3)_2C{=}CFCF_2CF_3$.[25] The reaction leads to the formation of $R_2N\underset{\underset{CF_3}{|}}{C}F{=}CFCF_2CF_3$, which may indicate a preliminary isomerisation of the dimers to $CF_2{=}\underset{\underset{CF_3}{|}}{C}(CF_2)_2CF_3$.[87] This result makes possible the extensive application in synthesis of the very readily available fluoro-olefin oligomers. Dialkylaminoheptafluoroisobutenes are also capable of reacting with secondary amines[88]:

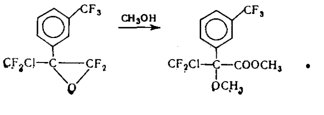


$$(CF_3)_2C{=}CFNR_2 + HNR'_2 \rightarrow (CF_3)_2C{=}C\begin{matrix}NR_2\\NR'_2\end{matrix}.$$

The reaction proceeds readily when R or R′ is a methyl group. When both substituents are a piperidine residue, the reaction proceeds slowly and, when $R = R' = C_2H_5$, it is altogether impossible to achieve selective substitution. Evidently steric hindrance plays a decisive role in this instance.

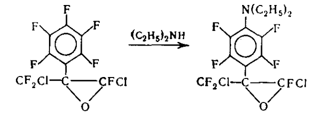
Steric hindrance plays an important role in the reactions of fluoro-oxirans with nucleophilic agents. In the absence of steric hindrance, the attack is directed to the central carbon atom[89,90]:

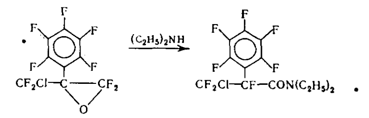




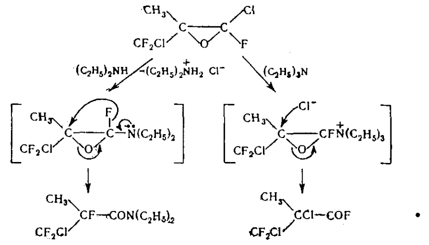
The second reaction takes place fairly readily when the CF_3 group is present in the *meta*- or *para*-position, but does not occur when it occupies the *ortho*-position[90].

The *ortho*-fluorine atoms of the pentafluorophenyl group are evidently also capable of shielding the central carbon atom sufficiently for the attack by the nucleophilic agent to be directed to another centre[90]:

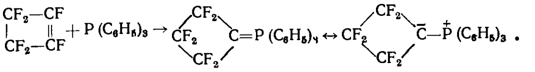




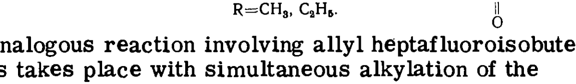
In the second case the reaction is accompanied by a rearrangement, which is of a general type. With its aid, it is possible to synthesise the derivatives of a wide variety of fluorocarboxylic acids. Evidently the driving force of the reaction is the small volume of the halide ions formed in the first stage of the interaction with bulky nucleophilic agents, which are bound to attack the terminal carbon atom[90]:



According to mechanism (2), the primary products of the reactions of fluoro-olefins with uncharged nucleophilic agents are dipolar species. In certain cases, these products can be isolated[91]:



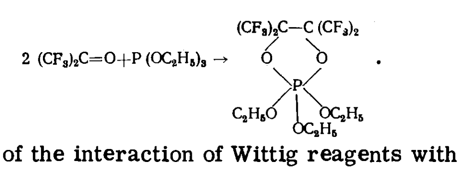
Heptafluoroisobutenylphosphonic acid esters have been obtained by the reaction between octafluoroisobutene and trialkyl phosphites (in which a betaine is an intermediate)[92]:



$$(CF_3)_2C{=}CF_2 + P(OR)_3 \rightarrow [(CF_3)_2\bar{C}{-}CF_2{-}\overset{+}{P}(OR)_3] \rightarrow (CF_3)_2C{=}CF{-}\underset{\underset{O}{\|}}{P}(OR)_2;$$
$$R{=}CH_3,\ C_2H_5.$$

The analogous reaction involving allyl heptafluoroisobutenyl ethers takes place with simultaneous alkylation of the trialkyl phosphite via mechanism (1).[93] The influence of steric hindrance, preventing the attack on the carbon atom of the =CF– group, probably has an effect in this case.

The reaction of triethyl phosphite with hexafluoroacetone is unusual. The addition of two ketone molecules results in the formation of a cyclic phosphorane in which there is a linkage between two carbon atoms previously forming part of the carbonyl groups, i.e. hexafluoroacetone is converted into a "pinacol" derivative[94]:



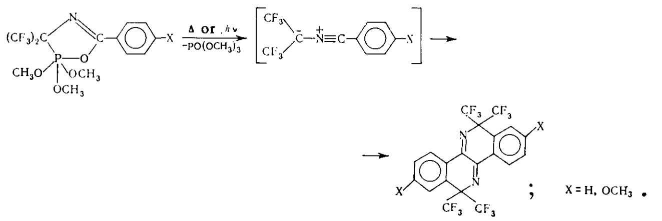
(3)

The study of the interaction of Wittig reagents with unsaturated organofluorine compounds, which was begun in relation to hexafluorobenzene [95], is extremely promising:

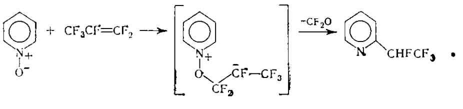
$$(C_6H_5)_3\overset{+}{P}{-}\bar{C}H_2 + C_6F_6 \rightarrow [(C_6H_5)_3\overset{+}{P}{-}CH_2C_6F_5[F^- \xrightarrow{-H^+} (C_6H_5)_3\overset{+}{P}{-}\bar{C}HC_6F_5.$$

The reaction leads to the formation of a new ylid, which is likewise capable of typical reactions of such compounds.

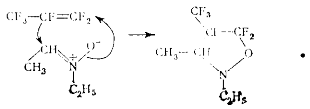
Nitrogen-containing ylids usually cannot be isolated, but the products of their reactions are frequently extremely interesting[96]:



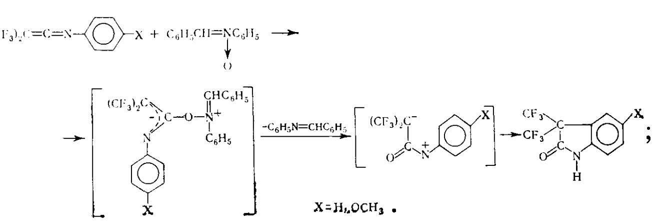
The reaction of the N-oxides of pyridine (and its homologues) with hexafluoropropene makes it possible to introduce the polyfluoroalkyl group under mild conditions into the α-position of the pyridine ring[97]:



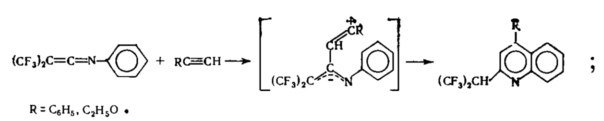
Nitrones also react steadily with hexafluoropropene, but there is no elimination of the COF_2 group[98]:



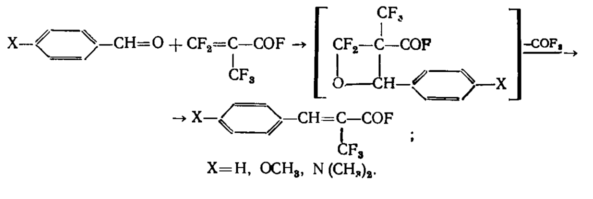
α,N-Diphenyl nitrone behaving as an oxygen donor reacts in an unexpected manner with N-arylbis(trifluoromethyl)ketenimines [99]:



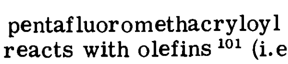
The reaction of a ketenimine with acetylenes probably also includes a stage involving the formation of a dipolar ion, which is stabilised by cyclisation[100]:



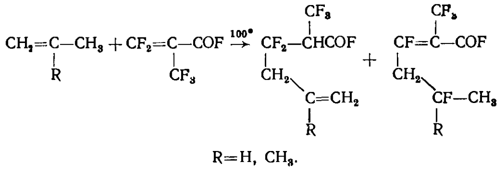
Another pathway to the stabilisation of the dipolar ion, involving the elimination of carbonyl fluoride, which has already been mentioned, occurs in the interaction of aromatic aldehydes with pentafluoromethacryloylfluoride. The intermediate oxetans are unstable[101]:



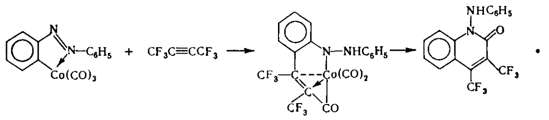
The extreme ease of this reaction, which is formally similar to the Wittig reaction, is not surprising if one bears in mind that both charges in the intermediate dipolar ions are highly delocalised, so that it constitutes a combination of the benzoyl cation with a mesomeric anion:



The C=C bond in pentafluoromethacryloyl fluoride is so electrophilic that it reacts with olefins[101] (i.e., as regards its electrophilic properties, it approaches the C=O bond of fluorinated ketones—see a previous review[1]):



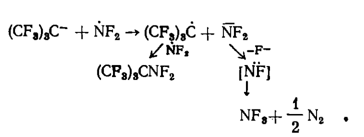
An example illustrating the extremely great promise of the use of transition metal complexes for the synthesis of organofluorine compounds is provided by the incorporation of hexafluorobut-2-yne in the cobalt complex of azobenzene accompanied by carbonylation[102]:



The intermediate complex has been isolated and its structure has been confirmed by X-ray diffraction.

4. New Ideas About the Mechanisms of Anionoid Processes

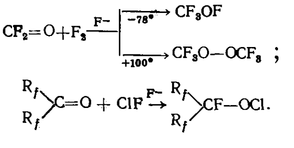
The reactions involving fluorocarbanions cannot always be accounted for within the framework of purely ionic concepts. For example, the interaction of octafluoroisobutene with tetrafluorohydrazine, resulting in the formation of $(CF_3)_3CNF_2$, is catalysed by KF. Since N_2F_4 decomposes on heating with formation of $\dot{N}F_2$ radicals, the decisive stage in the process is probably the oxidation of the carbanion $(CF_3)C^-$ by this radical[103]:



The "ionic" bromination of polyfluoroalkanes[104]:

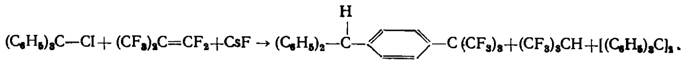
$$(CF_3)_3CH + Br_2 \xrightarrow[C_5H_5N]{} (CF_3)_3CBr$$

and the reactions of "perfluoroalkoxides" with halogens or interhalogen compounds[105,106]:



are just as likely to have oxidative mechanisms.

The ability of the fluorocarbanion to behave under mild conditions as an electron donor was confirmed directly in an ESR study of an unusual reaction between the nonafluoro-t-butyl anion and chlorotriphenylmethane involving the transfer of the reaction centre[107]:

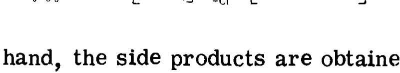


$$(C_6H_5)_3C{-}Cl + (CF_3)_2C{=}CF_2 + CsF \rightarrow (C_6H_5)_2\overset{H}{C}{-}C_6H_4{-}C(CF_3)_3 + (CF_3)_3CH + [(C_6H_5)_3C]_2.$$

At the beginning of the reaction, the concentration of the triphenylmethyl radical increases sharply, and then falls only gradually to the level corresponding to the equilibrium

$$2\,(C_6H_5)_3C^{\cdot} \rightleftarrows [(C_6H_5)_3C]_2 .$$

Thus the main reaction product is obtained as a result of the recombination within a cage of the radical pair formed via electron transfer:



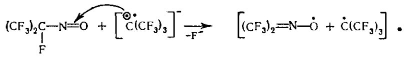
$$(C_6H_5)_3C{-}Cl + [\overset{\odot\cdot}{C}(CF_3)_3]^- \xrightarrow[-Cl^-]{} [(C_6H_5)\dot{C} + \dot{C}(CF_3)_3] .$$

On the other hand, the side products are obtained as a result of the liberation of the radicals from the "cage".

Yet another interesting reaction of carbanions, namely their reaction with nitroso-compounds, takes place with transfer of the reaction centre[108]:

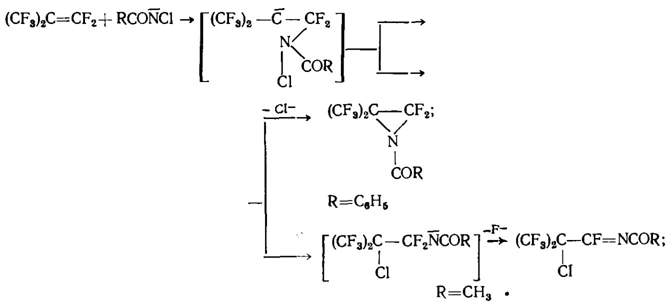
$$(CF_3)_2CF{-}NO + (CF_3)_2C{=}CF_2 \xrightarrow{CsF} (CF_3)_2C{=}NOC(CF_3)_3 .$$

Since it is known that in an aprotic medium fluoroalkylnitroso-compounds behave as one-electron oxidants (demonstrated by polarography in dimethylformamide[109]), this reaction presumably includes an electron transfer stage (otherwise it would be difficult to explain the attack by the carbanion on the oxygen atom rather than on the nitrogen atom):

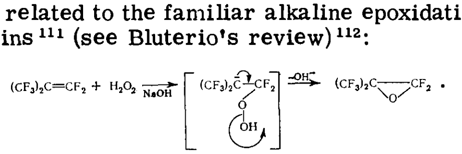


$$(CF_3)_2\underset{F}{C}{-}N{=}O + [\overset{\odot\cdot}{C}(CF_3)_3]^- \xrightarrow[-F^-]{} [(CF_3)_2{=}N{-}\dot{O} + \dot{C}(CF_3)_3] .$$

The reaction between octafluoroisobutene and *N*-chloramide anions can take place in two ways, depending on the nature of the acyl residue[110]:



The first, which is an example of the fixation of the intermediate of the Hofmann–Lossen rearrangements, is in essence related to the familiar alkaline epoxidation of fluoro-olefins[111] (see Bluterio's review)[112]:



The relation between the two pathways of the reaction with *N*-chloramides is the same as that between the Wurtz reaction and the metal halide exchange:

$$RLi + R'Cl - \begin{cases} \longrightarrow R{-}R' + LiCl \\ \longrightarrow RCl + R'Li \end{cases} .$$

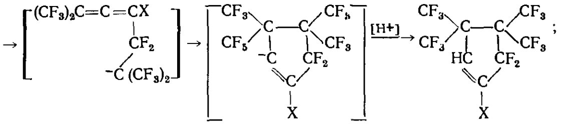
In both cases the key stage involves one-electron transfer[113].

The one-electron transfer stages evidently include also multistep transformations occurring when haloforms are added to a solution of the nonafluoro-t-butyl anion. The initial step is the generation of the trihalogenomethyl anion by virtue of the greater acidity of CX_3H (X = Cl or Br) compared with $(CF_3)_3CH$. The anion formed substitutes the vinyl fluorine atom in octafluoroisobutene:

$$(CF_3)_2C{=}CF_2 + \bar{C}X_3 \xrightarrow[-F^-]{} (CF_3)_2C{=}CFCX_3 \xrightarrow[-F^-]{CX_3^-} (CF_3)_2C{=}C{=}CX_2 + CX_4;$$

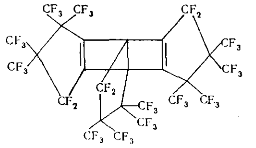
X=Cl, Br.

The dehalogenation of the resulting olefin takes place immediately afterwards, evidently under the influence of the trihalogenomethyl anion, which thus behaves as an electron donor. This leads to the formation of the carbon tetrahalide and an extremely electrophilic allene, which can be detected as an adduct with furan. In the absence of furan, the allene reacts with octafluoroisobutene via the following probable mechanism:



X=Cl, Br.

Thus an unusual conversion of octafluoroisobutene into a pinacol derivative takes place [cf. reaction (3)]. When X = Br, the cyclopentene formed is the final product. On the other hand, when X = Cl, the reaction proceeds further and a trimer is formed via an HCl elimination stage:



It was difficult to predict the formation of such final products on the basis of the structure of the initial reactants[114].

The reaction of bis(trifluoromethyl)thioketen with *NN*-dimethylaniline is accompanied by the formation of red intermediates, while the final product is $C_6H_5\underset{CH_3}{N}CH_2SCH{=}C(CF_3)_2$.[115] Presumably an electron transfer takes place in this case too, since the products of the substitution of the CH_3 group in *NN*-dimethylaniline are in fact usually formed as a result of one-electron oxidation of this amine, which readily gives rise to a radical-cation[116]. It is remarkable that other bases (alcohols, mercaptans, secondary amines) combine with bis(trifluoromethyl)thioketen via the C=C bond and not the C=S bond, i.e. the thioketen behaves as a normal acylating agent[115].

Yet another example of the "nucleophilic" reaction, the result of which is difficult to explain fully on the basis of purely ionic ideas, involves the dimerisation of bis(pentafluorophenyl)methyl bromide on treatment with cyanide ions or triphenylphosphine[117]:

$$2\,(C_6F_5)_2CHBr + CN^- \rightarrow (C_6F_5)_2CH{-}CH(C_6F_5)_2 + BrCN + Br^- .$$

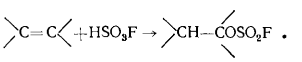
The product of this reaction is probably formed as a result of the recombination of the bis(pentafluorophenyl)methyl radicals.

A similar process is a side reaction in the substitution of pentafluorobenzyl chloride by butyl-lithium; it has been shown by physical methods that the reaction has a one-electron mechanism[118].

II. CATIONOID REACTIONS

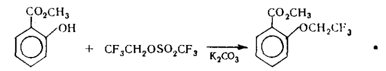
Owing to the presence of electron-accepting substituents in organofluorine compounds, their electrophilic reactions are more difficult than those of the non-fluorinated analogues. For this reason, either severe conditions or the use of very strong acids as the reaction medium are usually required in order to carry out such reactions successfully (see the review of Mochalina et al.[119]). On the other hand, the resistance of organofluorine compounds to severe conditions and strong acids, which cause charring of compounds, such, as for example, non-fluorinated olefins, makes their electrophilic reactions extremely valuable from the synthetic standpoint.

The simplest reaction occurring in strong protic acids is the formation of carbonium ions as a result of the protonation of organic molecules. The interaction of fluoro-olefins with fluorosulphonic acid has proved a convenient method for the synthesis of alkyl fluorosulphonates:



Fluoroethylenes react under extremely mild conditions[120] and tetrafluoroethylene and hexafluoropropene react under severe conditions, the products of their reactions being formed in low yields. α-Chloroperfluoroalkyl sulphonates are readily obtained by the addition of $ClOSO_2F$ to fluoro-olefins[121].

Alkyl fluorosulphonates are the strongest alkylating agents for *O*- and *N*-bases[122]. The reactivity of fluoroalkyl trifluoromethanesulphonates is just as high[123]:



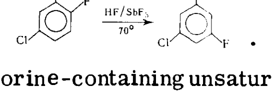
Remarkable prospects arise from the previously unknown ability of fluorosulphonates (other than methyl and ethyl fluorosulphonates) to function as *C*-alkylating agents for aromatic systems[120].

When fluoroethylenes are treated with the HF–SbF_5 mixture, they are hydrofluorinated. The reaction is reversible: the intermediate carbonium ion can be regenerated from the final products[124]:

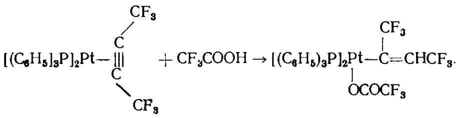
$$CH_2{=}CHF + HF + SbF_5 \rightleftarrows [H_3\text{—}\overset{+}{C}HF] \rightleftarrows CH_3\text{—}CF_2H.$$

Tetrafluoroethylene does not react in this way, which distinguishes it from ethylenes having the general formula $CF_2{=}CFX$, where X = Cl, Br, or I.

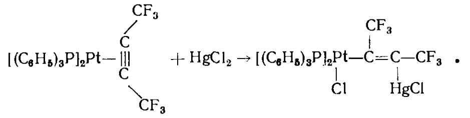
The benzenium ions formed on protonation of fluorobenzenes can be involved in rearrangements associated with the migration of both the proton[125] and the fluorine atom[126]:



The ability of fluorine-containing unsaturated compounds, coordinated to transition metals, to be protonated much more readily than in a free state is an extremely promising property. Thus, hexafluorobut-2-yne forming part of a platinum complex is readily protonated by trifluoroacetic acid[127]:

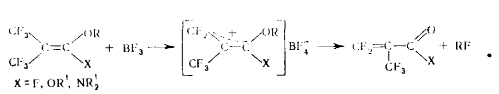


Evidently the range of electrophilic reactions of this kind can be greatly extended. Only the mercuration of this complex by mercury(II) chloride, an extremely mild mercurating agent, has been described so far[127]:



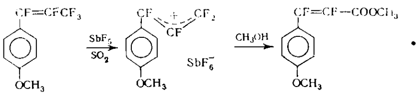
For comparison, one should note that the mercuration of perfluoro-olefins takes place only when the latter are heated with the much more active HgF_2 in HF or AsF_3 (see the review of Mochalina et al.[119]), while fluoro-olefins containing a hydrogen atom or an alkoxy-group at the C=C bond are mercurated by $Hg(NO_3)_2$.[128]

Carbonium ions are also formed when organofluorine compounds are treated with strong Lewis acids. It has been found that the fluorine atoms forming part of the CF_3 group of alkoxypolyfluoroisobutenes are sufficiently mobile for this purpose[129]:



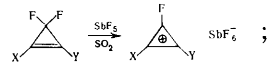
Salt-like intermediate products, containing a mesomerically stabilised cation, can be isolated after the reaction of the aminoacetals of bis(trifluoromethyl)keten (X = NR_2'). The final outcome of the reaction is the formation of derivatives of pentafluoromethacrylic acid and an alkyl fluoride.

On treatment with SbF_5, 4-pentafluoropropenylanisole also gives rise to a stable cation[130]:



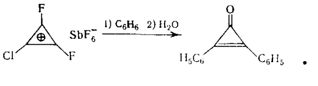
When the cation is treated with methanol, an ester of difluoro-*p*-methoxycinnamic acid is produced.

The salts containing fluorocycloprenyl cations do not decompose until a temperature near 80°C[131]:

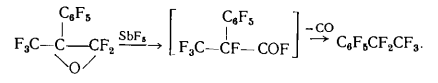


X, Y = F, Cl.

They are capable of alkylating benzene:

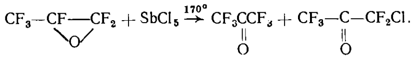


Owing to the ability of the acylium cations generated from carboxylic acid fluorides to eliminate CO, fluoroalkanes can be synthesised from the acids[132]. Oxirans, which are capable of being converted into acid fluorides under the influence of SbF_5, react similarly[90]:



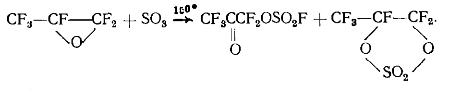
$$\underset{\text{O}}{F_3C\text{—}\overset{C_6F_5}{C}\text{—}CF_2} \xrightarrow{SbF_5} \left[F_3C\text{—}\overset{C_6F_5}{C}F\text{—}COF\right] \xrightarrow{-CO} C_6F_5CF_2CF_3.$$

The reactions of 1-trifluoromethyltrifluoro-oxiran catalysed by Lewis acids take place differently: antimony pentachloride converts it into a mixture of hexafluoro- and chloropentafluoro-acetones[133]:



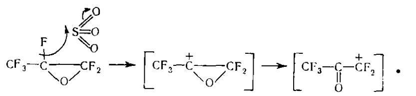
$$\underset{\text{O}}{CF_3\text{—}CF\text{—}CF_2} + SbCl_5 \xrightarrow{170^\circ} CF_3\underset{\|\atop O}{C}CF_3 + CF_3\text{—}\underset{\|\atop O}{C}\text{—}CF_2Cl.$$

Treatment with sulphur trioxide leads to the formation of two main products[133]:

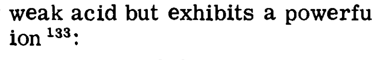


(4)

The hypothesis that Lewis acids can not only attack the oxiran at the oxygen atom, which results in the formation of the second product of reaction (4), but can be also coordinated to the fluorine atom of the CF group constitutes a very attractive explanation of these results:



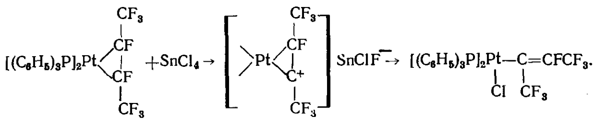
The rearrangement of the carbonium ion with subsequent attack by the anion on the CF_2 group can lead to substituted pentafluoroacetones. The validity of this hypothesis has been confirmed by the isolation of a certain amount of chloropentafluoroacetone in the reaction between 1-trifluoromethyltrifluoro-oxiran with SO_3 in the presence of NaCl. Furthermore, the oxiran is capable of an unexpected rearrangement in the presence of octafluoroisobutene, which is a very weak acid but exhibits a powerful affinity for the fluoride ion[133]:



The conversion of halogenofluoroalkanes into acid halides, catalysed by oleum, is based on the ability of SO_3 to be coordinated to a covalently linked halogen[134]:

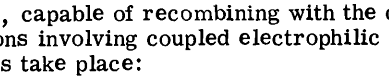
$$CF_2Br{-}CFClBr \xrightarrow[\text{oleum}]{} CF_2Br{-}COF.$$

The stage involving the formation of cations probably occurs also in the reaction of tin(IV) chloride with platinum complexes of fluoro-olefins[135]:



Reaction with the hexafluoropropene complex is accompanied by the exchange of the vinyl fluorine atom for chlorine, as a result of which the final product is $[(C_6H_5)_3P]_2Pt{-}\underset{\substack{|\\ Cl}}{C}Cl{=}CFCF_3$.

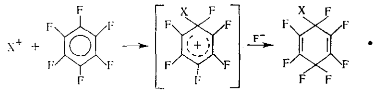
Carbonium ions are generated when a fluoro-olefin is attacked by cationoid species. When the medium contains fluoride ions, capable of recombining with the carbonium ions, reactions involving coupled electrophilic addition to fluoro-olefins take place:



X=NO_2, CH_2OH etc.

These processes, involving anhydrous hydrogen fluoride as a solvent and a source of F^- ions, have been reviewed in detail[136].

Aromatic fluoro-compounds are capable of similar reactions[137]:



Studies of such processes in other strong acids have developed in recent years. Thus, coupled fluorohalogenation of fluoro-olefins takes place readily in IF_5 [138] or BrF_3: [139]

$$CF_2{=}CF_2 + IF_5 + I_2 \rightarrow CF_3{-}CF_2I;$$
$$R_f{-}CF{=}CF_2 + BrF_3 + Br_2 \rightarrow R_f{-}CFBr{-}CF_3.$$

It is noteworthy that the last reaction is also undergone readily by hexafluoropropene dimers, which cannot be introduced into any other electrophilic addition reaction. The reaction involving the addition of chlorofluoroalkanes to fluoro-olefins, catalysed by the $AlCl_3$ (see the relevant reviews[119,140]), is related to these processes.

The results obtained using antimony pentafluoride as the reaction medium are particularly interesting. As already mentioned in a previous review[1], treatment of fluoroethylenes with this reagent leads to ready fluorination of the double bond. Polyfluoropropenes unexpectedly undergo electrophilic dimerisation[141]:

$$2\,CF_3{-}CX{=}CF_2 \xrightarrow{SbF_5} CF_3{-}CX{=}CF{-}CX\,(CF_3)_2;$$
$$X{=}H,\ F.$$

On the other hand, when hexafluoropropene reacts with SbF_3 in the presence of pentafluorobenzene, decafluoro-β-methylstyrene is formed[142]:

$$CF_3{-}CF{=}CF_2 + C_6F_5H \xrightarrow[SbF_5]{} C_6F_5{-}CF{=}CF{-}CF_3.$$

Pentafluorobenzene is alkylated also on treatment with 1,1,2-trichloro-1,2,2-trifluoroethane in SbF_5. The reaction is accompanied by the partial substitution of chlorine by fluorine, so that its main product is β-chlorononafluoroethylbenzene, from which octafluorostyrene can be readily obtained[143]:

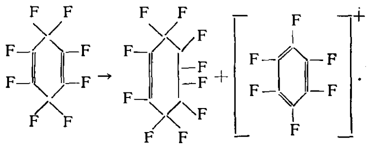
$$C_6F_5H + CF_2Cl{-}CFCl_2 \xrightarrow[SbF_5]{} C_6F_5{-}CF_2{-}CF_2Cl.$$

When vinylidene fluoride was allowed to react with SbF_5, it was possible to isolate an addition product[144]:

$$3\ CF_2{=}CH_2 + SbF_5 \rightarrow (CF_3CH_2)_3SbF_2.$$

The behaviour of fluoro-olefins in SbF_5 is at present difficult to account for unambiguously: possibly the fluorination of the double bond involves a stage where fluoroalkyl derivatives of antimony(V) are formed with subsequent elimination of SbF_5. Presumably the dimerisation of fluoropropenes also includes a stage in which organoantimony compounds are produced. However, the analogous dimerisation of 3,3,3-trifluoropropene occurs when it is acted upon by fluorosulphonic acid and not SbF_5. The intermediate formation of the difluoroallyl cation in this reaction with its subsequent rearrangement to the final dimer has been suggested[145].

However, the dimerisation of hexafluoropropene or its reaction with C_6F_5H can be satisfactorily accounted for by assuming the formation of the vinyl cation $CF_3CF{=}CF^+$. Moreover, one must not fail to take into account the oxidising properties of SbF_5. Thus hexafluorobenzene forms a stable radical-cation in antimony pentafluoride.[146] The same radical-cation has been detected when SbF_5 was allowed to react with octafluorocyclohexa-1,4-diene, which also leads to the formation of decafluorocyclohexene—the disproportionation product[147]:



In principle, one cannot rule out the involvement of one-electron transfer processes also from the above reactions of fluoro-olefins, the study of which is being continued.

The oxidising properties of SbF_5 play a decisive role in the recently developed method for the synthesis of organofluorine derivatives of Group VI elements (sulphur, selenium, and tellurium). The method is based on the ability of these elements to form in SbF_5 the double charged cations E_n^{2+} (n = 4, 8, or 16).[148] When these solutions are allowed to react with fluoro-olefins, disulphides or diselenides are formed[149,150]:

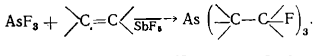
$$CF_3{-}CF{=}CF_2 + E_n^{2+}\cdot 2SbF_6^- \xrightarrow[SbF_5]{} (CF_3)_2CF{-}E{-}E{-}CF(CF_3)_2;\quad E = S, Se.$$

When sulphur reacts with pentafluorobenzene in SbF_5, substitution takes place[151]:

$$C_6F_5H \xrightarrow[SbF_5]{S} (C_6F_5)_2S.$$

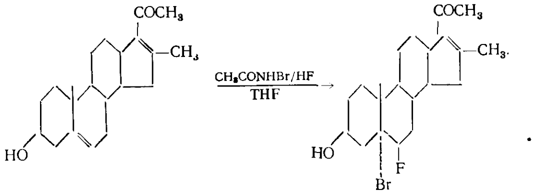
Similar results have been obtained when the pure salts $S_8(AsF_6)_2$,[152] $Se_8(AsF_6)_2$,[153] and $Te_4(AsF_6)_2$ [154] were used instead of the solutions. The products of the reactions with tetrafluoroethylene are the corresponding organic derivatives of the elements, hexafluoroethane being formed as a side product.

Antimony pentafluoride in catalytic amounts effectively promotes the addition of arsenic trifluoride to fluoro-olefins[155]:



Sulphur trioxide reacts with fluoro-olefins just as readily as SbF_5, with formation of β-sultones, the chemistry of which has been reviewed[156].

Together with studies on new synthetic possibilities, arising from the application of highly reactive reagents, the development of mild synthetic methods suitable, for example, for physiologically active substances, is important. Thus the use of hydrogen fluoride diluted with tetrahydrofuran as the medium for coupled fluorobromination makes it possible to involve in the reaction only one (more reactive) double bond of 16-methylpregnadiene[157]:



The use of hydrogen fluoride in pyridine as the medium constitutes a significant improvement, permitting reactions involving coupled addition to systems which are unstable in anhydrous hydrogen fluoride[158]. A mild version of fluorohalogenation involves treatment of unsaturated compounds with iodine or bromine in the presence of AgF.[159]

The addition of $(CF_3)_2N{-}X$ (X = Cl, Br, or I) [160] or SF_5Br [161] to fluoro-olefins, the direction of which corresponds to electrophilic addition, should be nevertheless probably classified as a radical process, the direction of which is associated with the pronounced electrophilic properties of the attacking radicals[1]. The stereospecificity of the addition of $(CF_3)_2N{-}X$ (X = Cl or Br) to *cis*- and *trans*-butenes (*trans*-addition[162]) does not constitute exhaustive proof of an ionic process mechanism, since the addition of fluoroalkyl iodides to cyclopentene under the conditions of a radical reaction also leads exclusively to the *trans*-adduct[163].

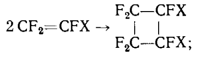
III. RADICAL REACTIONS

Both free-radical processes and reactions to which a latent radical mechanism can be attributed will be considered in this section. Since the latter reactions frequently include thos which have been treated previously as purely "ionic", the assignment of a process to the series of "ionic" or "radical" reactions is in many cases based merely on a traditional classification.

The radical reactions of organofluorine compounds are frequently distinguished by high selectivity, which makes them valuable in syntheses. Thus, using a radical process, it has proved possible to ("liven") activate fluoroalkanes containing the CF_2H group, which were regarded as inert with respect to any influences under mild conditions[164]:

$$n\text{-}C_3F_7H + FSO_2O{-}OSO_2F \xrightarrow[60-70°]{} n\text{-}C_3F_7OSO_2F.$$

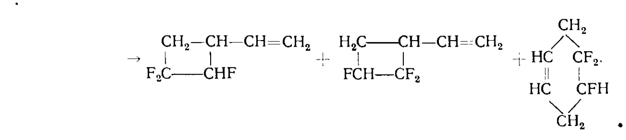
Cycloaddition processes belong to radical reactions of unsaturated organofluorine compounds which are of preparative value. The cyclodimerisation of fluoro-olefins, occurring readily on heating, proceeds very specifically: two molecules of an asymmetrically substituted olefin always combine "head to head":



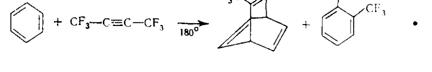
$$2\,CF_2{=}CFX \rightarrow \begin{array}{l} F_2C{-}CFX \\ \;\;|\qquad\;\; | \\ F_2C{-}CFX; \end{array}$$

$X = Cl^{165}$, $C_6H_5^{166}$.

The direction of cycloaddition indicates its "non-concerted mechanism", i.e. the involvement in the reaction of a stage where biradicals are formed, the formation of biradicals of the type $X\dot{C}FCF_2CF_2\dot{C}FX$, with a higher degree of delocalisation of electrons, being preferable[165,167]. The addition of tetrafluoroethylene to ethylene and to *cis*- and *trans*-butenes is also a non-concerted process[168]. However, when trifluoroethylene adds to 1,3-dienes, there is evidence of competition between two process mechanisms—a non-concerted mechanism leading to "2 + 2" addition and a concerted mechanism, which results in "2 + 4" addition[169,170]:

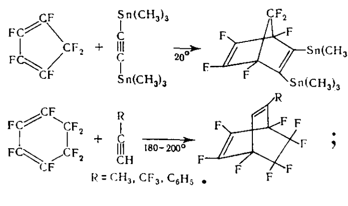


Hexafluorobut-2-yne, which has an extremely electrophilic triple bond, reacts as a dienophile even with aromatic hydrocarbons[171]:



At a higher temperature, bicyclic adducts can not be isolated and poly(fluoroalkyl)benzenes become the main reaction products. The process thus reduces to the substitution of acetylene by hexafluorobut-2-yne. When the same starting materials are irradiated with ultraviolet light in the gas phase, the main reaction product is 1,2-bis(trifluoromethyl)cyclo-octatetraene.[171]

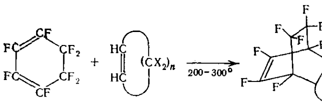
Fully fluorinated cyclic 1,3-dienes are also capable of involvement in diene synthesis[172,173]:



(5)

Pyrolysis of the products of reaction (5) leads to the elimination of C_2F_5 and the formation of substituted 1,2,3,4-tetrafluorobenzenes.[173]

Octafluorocyclohexadiene adds also to cyclo-olefins [174]:



X = H, F; n = 2–4 .

Reactions using fluoroalkyl radicals generated by electrochemical methods are of preparative interest, since readily available carboxylic acids can then be used as the starting compounds. The simplest process occurring in the electrolysis of acids is the Kolbe reaction, for example[175]:

$$2\,(CF_3)_2CH{-}CO_2H \xrightarrow[\text{Pt anode}]{} (CF_3)_2CH{-}CH(CF_3)_2 + 2CO_2.$$

The resulting product is a convenient starting compound for the synthesis of decafluoro-2,3-dimethylbutadiene.

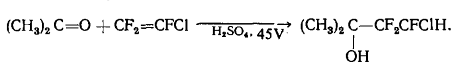
In the presence of agents capable of reacting with a radical, the Kolbe synthesis is suppressed, which leads to many interesting possibilities[176,177]:

$$\begin{gathered} CF_3COOH + Br_2 \xrightarrow[\text{anode}]{} CF_3Br + CO_2; \\ CF_3COOH + H_2O \xrightarrow[\text{anode}]{} CF_3{-}O{-}O{-}CF_3 + CO_2. \end{gathered} \tag{6}$$

It is noteworthy that, under certain electrolysis conditions, an unexpected product of reaction (6) (a peroxide) is obtained in yields up to 80%. Its formation is caused by the fact that the oxidation potential of water is somewhat lower than that of trifluoroacetic acid. Hexafluoroethane, the "normal" reaction product, becomes an impurity (together with trifluoromethyl ether).[177]

Interesting possibilities arise from the "mixed" version of the Kolbe reaction. Thus joint electrolysis of propionic and trifluoroacetic acids gave 3,3,3-trifluoropropene in 23% yield (in a mixture with other products). The authors[178] suggest that the formation of an unsaturated product is caused by the preliminary dehydrogenation of propionic acid, leading ultimately to ethylene, which actually reacts with the $\dot{C}F_3$ radical.

The condensation of acetone with chlorotrifluoroethylene, a cathodic process, is likewise of interest[179]:



$$(CH_3)_2C{=}O + CF_2{=}CFCl \xrightarrow[H_2SO_4,\ 45V]{} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CF_2CFClH.$$

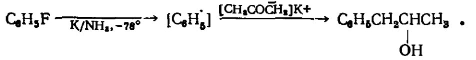
Evidently the species attacking the C_2F_3Cl molecule is the fairly stable radical $(CH_3)_2\dot{C}OH$, formed as a result of the protonation of the acetone ketyl.

Electrochemical reduction of the CF_3 group linked to an aromatic ring cannot be stopped at the stage involving the formation of the CHF_2 or CH_3F group when there is a methoxycarbonyl group in the *meta*- or *para*-position. Two different mechanisms then operate—a one-electron reversible mechanism for the *meta*-isomer and a two-electron irreversible mechanism for the *para*-isomer (cyclic voltammetry [180]).

The reduction of fluorine atoms linked to the benzene ring is facilitated as they accumulate. Each fluorine atom in pentafluorobenzene is reduced in a one-electron irreversible process via the following mechanism[181]:

$$ArF \xrightarrow{e} [ArF]^{\cdot} \xrightarrow{H+} [ArFH]^{\cdot} \xrightarrow{e} [ArFH]^{-} \xrightarrow{-F^-} ArH.$$

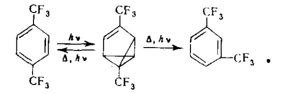
The first reduction product of pentafluorobenzene is 1,3,4,5-tetrafluorobenzene, i.e. the hydrogen atom is introduced in the *meta*-position relative to that already present and the direction of substitution is similar to that observed in nucleophilic reactions[181]. The reduction of fluorobenzene is difficult, but potassium in liquid ammonia causes it to react with potassium acetonate[182]:



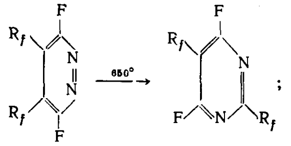
$$C_6H_5F \xrightarrow[K/NH_3,\ -78^{\circ}]{} [C_6\dot{H}_5] \xrightarrow{[CH_3CO\bar{C}H_2]K+} C_6H_5CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 .$$

Even a Grignard reagent can be synthesised from fluorobenzene with the aid of specially prepared highly reactive magnesium (admittedly in a low yield)[183].

As already mentioned[1], when aromatic fluoro-compounds are irradiated with ultraviolet light, their valence isomers are readily formed. When the aromatic ring contains fluoroalkyl groups, irradiation leads to rearrangements including a benzvalene formation stage[184]:

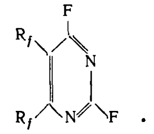


The reaction has a low quantum yield. Similar rearrangements occur also in the series of heterocycles at high temperatures[185]:

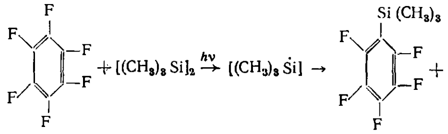


$R_f = (CF_3)_2CF$— .

When $R_f = C_2F_5$, there is no migration of the fluoroalkyl group and the following compound is formed:

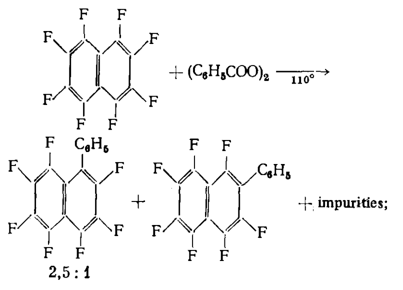


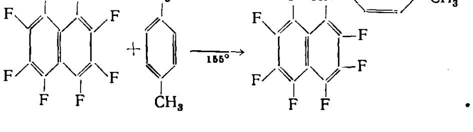
A new type of photochemical reaction of aromatic fluoro-compounds is substitution or addition involving C–F bonds, for example[186]:



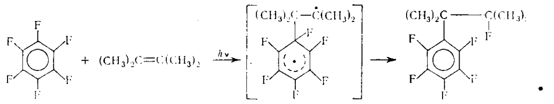
$$+ [(CH_3)_3Si]_2 \xrightarrow{h\nu} [(CH_3)_3\dot{S}i] \rightarrow \ldots + (CH_3)_3SiF + 1.3\text{- и } 1.4\text{-}[(CH_3)_3Si]_2C_6F_4.$$

Similar reactions occur also on thermal generation of radical species[187,188]:

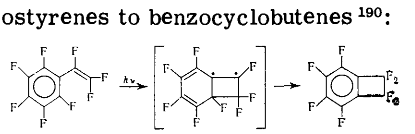




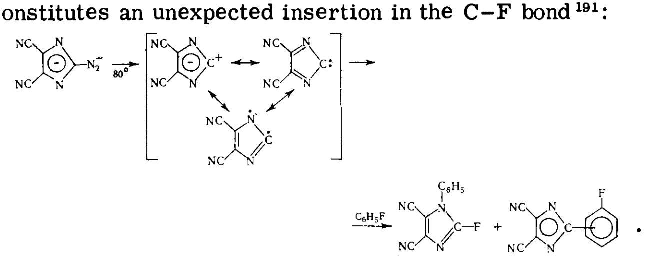
On ultraviolet irradiation, olefins are capable of being "inserted" in the C–F bond[189]:



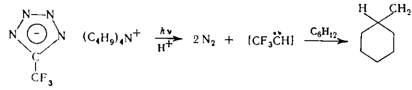
An intramolecular version of this reaction is the cyclisation of polyfluorostyrenes to benzocyclobutenes[190]:



The reaction of fluorobenzene with an extremely interesting carbene having the overall formula C_5N_4 constitutes an unexpected insertion in the C–F bond[191]:



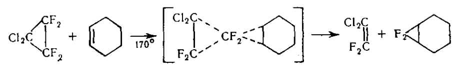
The search for new convenient sources of carbenes is a characteristic feature of research in the chemistry of these species (see Hoffmann's review[192]). Organosilicon ($CHF_2CF_2SiF_3$)[193] or organomercury ($CF_3HgOCOCF_3 + NaI$)[194] compounds are accessible sources of fluorine-containing carbenes. The ready decomposition, promited by iridium complexes, of $CF_2ClCOONa$, which is a traditional source of difluorocarbene, holds out some promise. The only reaction products isolated were iridium compounds, in particular $ClCF_3COO\underset{\underset{CF_2H}{|}}{Ir}(CO)[P(C_6H_5)_3]_2$. Research on its synthetic applications is being continued[195]. Fluorine-containing carbenes are readily generated also with the aid of photochemical reactions[196,197]:



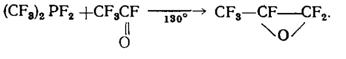
$$CF_2{=}N{-}N{=}CF_2 \xrightarrow{h\nu} CF_2{=}N{-}CF_2{-}N{=}CF_2\ .$$

In the latter case the source of the carbene itself plays the role of a carbene trap[197].

Another source of difluorocarbene employed is 1,1-difluorocyclopropanes—the products of the addition of difluorocarbene to olefins. It is remarkable that the transfer of carbene takes place under milder conditions than the decomposition of the cyclopropane in the absence of the other reactant. This suggests that the transfer proceeds without the formation of a kinetically independent carbene and constitutes "nucleophilic substitution" at the CF_2 group. The reaction takes place with a quantitative yield[198]:

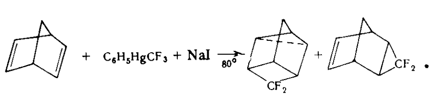


1-Trifluoromethyltrifluoro-oxiran, a widely used source of CF_2, can also be obtained from trifluoroacetyl fluoride—its usual decomposition product[199]:

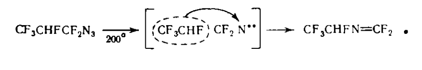


$$(CF_3)_2PF_2 + CF_3\underset{\underset{O}{\|}}{C}F \xrightarrow[130^\circ]{} CF_3{-}CF{-}CF_2\ (\text{—O— bridge}).$$

Owing to the weak electrophilic properties of difluorocarbene, it has been possible to cause its addition to norbornadiene in an unusual manner[200]:

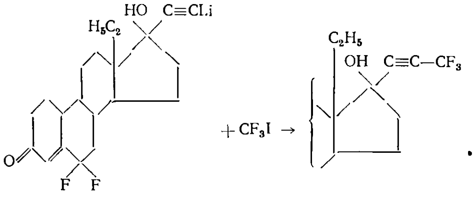


Fluoroalkylnitrenes, formed in the thermolysis of the corresponding azides, undergo a rearrangement analogous to the Curtius rearrangement. This finding illustrates the similarity between the CF_2 and C=O groups[201]:

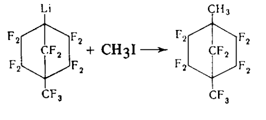


$$CF_3CHFCF_2N_3 \xrightarrow[200^\circ]{} \left[CF_3CHF\,CF_2N^{\cdot\cdot}\right] \longrightarrow CF_3CHFN{=}CF_2\ .$$

Reactions involving the single-stage introduction of a polyfluoroalkyl group into an organic molecule are extremely important from the preparative point of view. Certain examples of such reactions have been examined in previous sections, but they were not general. The simplest method for combining hydrocarbon and fluorocarbon residues, namely the Wurtz reaction, does not occur in many cases: when organomagnesium compounds, for example, interact with fluoroalkyl iodides, there is only metal halide exchange[45], caused by the large difference between the electronegativities of the fluoroalkyl and alkyl groups[113]. However, acetylides are probably capable of substituting iodine in fluoroalkyl iodides[203]:



The reason for this mode of reaction may be the high electronegativity of carbon in the *sp*-hybridised state. Other examples of this reaction are not quoted in the literature. The "opposite" case—the Wurtz reaction between fluoroalkyl derivatives of lithium and methyl iodide—is apparently specific to the bicyclic system involved in it[203]:



An unusual method for the introduction of a fluoroalkyl group into ferrocene has been described in a patent[204]:

$$(C_5H_5FeC_5H_4)_2Hg + C_3F_7I \xrightarrow[100^\circ,\ C_6H_6]{} C_5H_5FeC_5H_4C_3F_7\ .$$

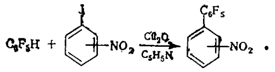
Since the reaction is unknown for other organomercury compounds, presumably the reducing properties of the iron atom forming part of ferrocene play an important role in this case. This hypothesis is supported by the finding that reactions of the type of the Wurtz reaction (RMgBr + R′Br) are effectively promoted by transition metal salts (silver or copper salts) and also (for R = alkenyl) by metallic iron[205].

The recently described synthesis of fluorine-containing ketones is a related process. The reaction is catalysed by a carbonylate anion:

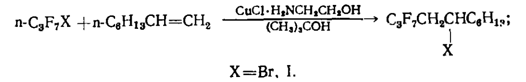
$$n\text{-}C_7H_{15}COCl + Br(CH_2)_6CN \xrightarrow[Na_2Fe(CO)_4]{} C_7F_{15}CO(CH_2)_6CN.$$

Not only acyl chlorides but also fluoroalkyl bromides can be used as the starting compounds. In this case the carbonylate serves as a source of CO.[206]

However, univalent copper is a particularly effective and widely used catalyst. Thus, in the presence of copper(I) oxide, pentafluorobenzene is readily arylated[207]:



Fluoroalkyl halides add to olefins under mild conditions when the reaction is catalysed by a CuCl complex with ethanolamine. The reaction takes place with a high yield and is not accompanied by telomerisation[208]:



$$n\text{-}C_3F_7X + n\text{-}C_6H_{13}CH{=}CH_2 \xrightarrow[(CH_3)_3COH]{CuCl\cdot H_2NCH_2CH_2OH} C_3F_7CH_2\underset{\displaystyle X}{\underset{|}{C}}HC_6H_{13};$$

$X{=}Br, I.$

Copper can be involved in electrophilic cooperation in the substitution of a halogen other than fluorine in the compounds C_6F_5X (X = Br or I). In the absence of copper, only fluorine undergoes nucleophilic substitution by alcohols, amines, or mercaptans, but in its presence the mode of reaction changes completely. Thiourea, which binds copper, restores the usual mode of reaction[209]:

$$C_6F_5Br + C_4H_9SCu \xrightarrow[(CH_3)_2NCHO]{} \begin{cases} \xrightarrow{\qquad} C_6F_5SC_4H_9 \\ \xrightarrow[4(NH_2)_2C=S]{} n\text{-}C_4H_9SC_6F_4Br. \end{cases} \qquad (7)$$

The reaction with secondary amines in the presence of CuBr involves the reduction of the C–Br bond together with the substitution of fluorine[209].

Evidently the catalytic activity of univalent copper is due to its ability to be oxidised by transferring an electron to the C–Br or C–I bond. Copper forming part of fluoroalkyl derivatives, which are fairly resistant to heat and hydrolysis, probably retains this ability (see Normant's review[210]). These compounds are readily obtained by the general method for the synthesis of many organometallic derivatives—the reaction between the metal and the halide. In the series of organofluorine derivatives, the reaction is used for a particularly wide range of elements[211-213]:

$$R_fI + M \to R_fM + MI;$$
$$R_f{=}n\text{-}C_3F_7,\ n\text{-}C_7F_{15},\ M{=}Cu;$$
$$R_f = C_6F_5,\quad M = \frac{1}{2}Zn,\ Cd.$$

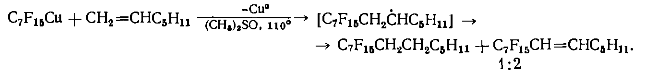
Other examples are quoted in a previous review[1].

Fluoroalkyl derivatives of copper are capable of adding to olefins, which results in the formation of a mixture of alkanes and alkenes[214]:

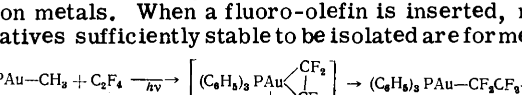
$$C_7F_{15}Cu + CH_2{=}CHC_5H_{11} \xrightarrow[(CH_3)_2SO,\ 110°]{-Cu^0} [C_7F_{15}CH_2\dot{C}HC_5H_{11}] \to$$
$$\to C_7F_{15}CH_2CH_2C_5H_{11} + C_7F_{15}CH{=}CHC_5H_{11}.$$

1:2

This reaction probably includes a "*cis*-insertion" stage, which is common to many reactions of σ-derivatives of transition metals. When a fluoro-olefin is inserted, new σ-derivatives sufficiently stable to be isolated are formed[215]:



A similar stage may be involved also in the fluoroalkylation of halogeno-olefins by copper compounds[214]:



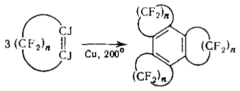
$R_f{=}C_3F_7,\ C_7F_{15}.$

Another explanation is that copper is merely involved in electrophilic cooperation in the substitution of a halogen by the R_f anion, as in reaction (7).[216]

All these processes closely resemble the classical Ullmann reaction, whose "mixed" version can be very successfully achieved using fluoroalkyl derivatives of copper:

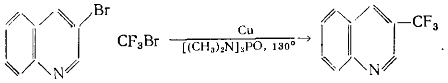
$$R_fHal + RHal \to R_f{-}R.$$

Since RHal is added to a previously prepared solution of R_fCu, the formation of $R_f{-}R_f$ or R–R is ruled out[217,218]. A novel method for the synthesis of an aromatic system has been described in a patent[219]:



$n = 2, 3$.

A particularly valuable feature is that the Ullmann reaction makes it possible to introduce a fluoroalkyl group into heterocyclic compounds and it has been found that fluoroalkyl bromides, which are much cheaper than the iodides, can be used as a source of such groups[220]:



Under more severe conditions, a fluoroalkyl group can be introduced into the benzene ring, substituting a hydrogen atom, with the aid of fluoroalkyl derivatives of copper. The reaction evidently has a free-radical mechanism[221].

ADDENDUM

During the preparation of the review for the press, a number of new publications of significant interest appeared. Among these, mention should be made of a two-volume edition[222], which is a valuable compilation of studies in organofluorine chemistry published during 1969–1972. Another publication is a book entitled "Ftorpolimery" (Fluoro-Polymers)[223], which includes, among others, an extensive chapter devoted to the synthesis and properties of fluorine-containing monomers. In addition, data concerning the thermal stabilities[224] of fluoro-polymers and their resistance to benzene and oils[225] have also been reviewed. Among other new reviews, mention should be made of a paper[226] devoted to fluorine-containing medicinal preparations, a compilation of data[227] concerning the applications of fluorocarbon emulsions as blood substitutes, a review[228] of the valence isomers of aromatic poly(fluoroalkyl) compounds, and a paper[229] containing data on the silylation reactions of certain organofluorine compounds. A paper by Liebman[230], containing an extensive compilation of data on nucleophilic substitution reactions directed to the fluorine atom, is also of interest.

New data concerning the influence of the CF_3 group on the benzene ring to which it is linked have been obtained[231] by photoelectronic spectroscopy. The wide scope of this research technique in the study of organofluorine compounds has been demonstrated by an investigation[232] in which the structure of the hexafluorocyclobutene trimer has been proved with its aid and also in a study[233] where the method has been used to investigate thin layers of fluoro-polymers obtained photochemically on supports.

A number of new studies of the properties of the fluoride ion have been published. Thus a new version of the synthesis of alkyl fluorides has been proposed: by treating alkyl trifluoromethylsulphinates with caesium fluoride[234]. A method suggested[235] for increasing the reactivity of KF and also its solubility in aprotic solvents (acetonitrile, benzene) with the aid of a macrocyclic complex-forming agent (18-crown-6) also apparently gives rise to important possibilities. The geometry of the hydrogen fluoride ion has been studied[236]. A paper[237] is devoted to the anodic oxidation of *para*-disubstituted benzenes in the presence of the fluoride ion.

Reactions involving the elimination of the fluoride ion from organic molecules have been investigated[238,239]. The first study is devoted to the unusual reaction of polyfluorinated aldehydes with hydrazines, leading to the formation of alkazones. In the second study, an extremely convenient agent is proposed for the dehydrofluorination of polyfluorinated hydrocarbons—the complex $(C_2H_5)_3N.BF_3$. Derivatives of pentafluoromethacrylic acid can be readily synthesised with its aid[239]. The reactions of these derivatives with amines[240], isonitriles[241], and trialkyl phosphites[242] have also been investigated. The last reaction constitutes an unusual version of the substitution of vinyl fluorine atoms by alkoxy-groups. Among other studies in the chemistry of highly electrophilic organofluorine compounds, mention should be made of an investigation[243] of the synthesis and properties of 6,6-bis(trifluoromethyl)fulvene. A paper[244] deals in detail with the reaction of octafluoroisobutene with haloforms in the presence of CsF. New electrophilic olefins (perfluoromethylenecyclopropane[245]) and also ethylenes containing the CF_3SO_2 group[246] have been investigated.

A study has been made of the synthesis and properties of acetylene containing the same substituent[247].

The reactions of fluoro-olefins with nucleophilic agents have been the subject of a study[248] in which the erroneous results of studies by earlier workers, who investigated the reactions of fluoro-olefins with sodiomalonic ester have been revised, a study dealing with the addition-elimination mechanism in nucleophilic reactions[249], and also a study[250] where the radical and ionic pathways in the reactions between fluoro-olefins and phosphines are considered. The characteristics of nucleophilic substitution in perfluoromesitylene are discussed by Markov et al.[251]

A number of studies have been devoted to fluorine-containing organometallic compounds: that of Nefedov et al.[252], who investigated the mechanism of the elimination of LiF by the *o*-fluorophenyl-lithium ether adduct, a study by Fedorov et al.[253] of the stoichiometry of the solvation of fluoroalkyl derivatives of mercury (by NMR), and a study[254] where an unusual type of thermal decomposition of 1,6-di(bromomagnesio)dodecafluorohexane, leading to high yields of decafluorocyclohexene, has been demonstrated. The syntheses of a number of fluorine-containing β-diketones—analogues of thenoyltrifluoroacetone which are promising complex-forming agents—have been described[255].

New reactions of fluorine-containing oxirans have been investigated—their synthesis form α-substituted difluoroacrylic acids[256] and the interaction of oxirans with azides[257] and lithium aluminium hydride[258]. In addition the mode of the opening of the oxiran ring has been studied as a function of the catalyst employed and the reaction conditions[259].

Among investigations devoted to electrophilic reactions of fluoro-olefins, mention should be made of those concerned with the reactions of metastable enols of polyfluoroacetones[260] (see Bekker et al. for the synthesis of the enols[261]). The behaviour of polyfluorinated 1,3-dienes under the conditions of ionic halogenation has been studied[262]. It is remarkable that the authors demonstrated the tendency of these compounds towards 1,4-addition. The alkenylation of aromatic polyfluoro-compounds by hexafluoropropene[263] and by polyfluorinated arenonium ions[264] (the generation of these ions has been described[265]) has been studied in detail. The remarkable ability of the SO_2–SbF_5 mixture (usually employed merely as a catalyst of electrophilic processes) to serve as an agent for introducing the SO_2 group into organic molecules has been discovered[266].

New radical reactions involving the addition of CF_3–O–O–Cl[267] and CF_3–S–S–Cl[268] to fluoro-olefins under mild conditions have been described[268]. The directions and rates of reaction have been studied in relation to the addition of CBr_4 and $CHBr_3$.[269] The high-temperature reaction between trifluoroiodoethylene and sulphur leads to a dimeric product: tetrafluorodithiosuccinyl fluoride[270]. It has been established that the free radicals $C_2F_5^{\cdot}$ react with hexafluorobenzene, forming a mixture of isomers of 4,4′-diethylperfluorotetrahydrobiphenyl.[271] A novel method for the generation of CF_3 radicals by the action of a glow discharge on hexafluoroethane enabled Lagow et al.[272] to synthesise in high yields derivatives of mercury, tellurium, tin, and germanium fully substituted by CF_3 groups. The photochemical generation of the CF_3 group from CF_3I permitted the synthesis of α-fluoroalkyl ketones from enamines[273]. The photolysis of CF_3I in the presence of benzene derivatives leads to substituted trifluoromethylbenzenes; the direction of substitution has been studied[274]. Among other photochemical reactions, mention should be made of an elegant synthesis of tetrakis(trifluoromethyl)cyclobutadiene dimer from the ozonide of hexakis(trifluoromethyl)benzvalene[275]. The selectivity and kinetics of the addition of difluorocarbene to substituted styrenes have been investigated[276].

The research on a very promising method for the introduction of fluoroalkyl groups into organic molecules with the aid of organocopper compounds by a reaction of the Ullmann type (a new review of this reaction has been published[277]) is being continued. Methods for the synthesis of acids and alcohols[278] and alkynes[279] containing fluoroalkyl groups have been developed on the basis of products obtained by the substitution of bromine in bromoalkenes. Interesting results have been obtained in a study of the reactions of fluoroalkylcopper compounds with 1-bromo-1-fluoroalkylethylenes[280]. Unexpectedly, this results in the formation of 1,2-bis(fluoroalkyl)ethylenes, i.e. the substitution of bromine takes place with transfer of the reaction centre, which suggests the involvement of the copper *d* electrons in the intermediate stages of the process.

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*Here and henceforth an asterisk denotes data quoted after the "Ftor" (Fluorine) IPS [the significance of the abbreviation is obscure (Ed. of Translation)] publication.

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Derivatives of Perfluoromethacrylic Acid

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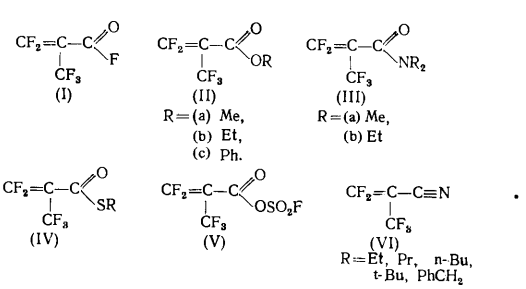
Methods for the synthesis and the chemical properties of perfluoromethacrylic acid derivatives are examined. The most characteristic reactions of these compounds are those with nucleophiles, including very weak nucleophiles; cycloaddition reactions are very common, and some perfluoromethacrylic acid derivatives polymerise and copolymerise with various unsaturated compounds.
The bibliography includes 83 references.

CONTENTS

I. INTRODUCTION

The comparatively ready availability and high reactivity of derivatives of $\alpha\beta$-unsaturated fluorine-containing carboxylic acids are responsible for the understandable interest shown in these compounds by investigators working in the fields of both pure and applied chemistry of organofluorine compounds. Derivatives of perfluoromethacrylic acid (**PFMA**) proved to be particularly reactive. Vigorous studies on compounds belonging to this class did not begin until very recent years, but during this short period it has proved possible to demonstrate the wide variety of their reactions and their synthetic possibilities. One cannot rule out the possibility that some **PFMA** derivatives may be used as monomers.

PFMA itself and its salts have not so far been obtained. It is quite likely that these compounds (particularly the salts) are altogether incapable of existence, since their molecules would contain simultaneously a nucleophilic centre (the COOH or COO^- group) and the highly electrophilic group $CF_2{=}C(CF_3)$. However, PFMA derivatives have been described in the literature: the acid fluoride (**I**), esters (**II**), dialkylamides (**III**), esters of the corresponding thiolo-acid (**IV**), the mixed anhydride of **PFMA** and fluorosulphonic acid (**V**), and perfluoromethacrylonitrile (**VI**).



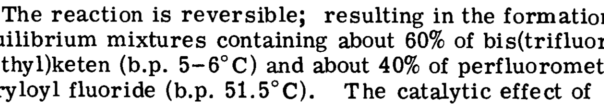
This review describes methods for the synthesis of these derivatives and their chemical reactions.

II. METHODS OF SYNTHESIS

The high reactivity of **PFMA** derivatives as a rule precludes the use for their synthesis of the usual synthetic methods for perfluoro-olefins or perfluorocarboxylic acid derivatives. In most cases it has been necessary to develop special methods (or special procedures) in order to obtain these compounds.

1. The Isomerisation of Bis(trifluoromethyl)keten

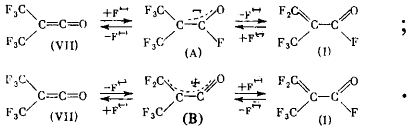
The first **PFMA** derivative, the acid fluoride (**I**), was obtained by the isomerisation of the comparatively readily available bis(trifluoromethyl)keten (**VII**):[1]



$$(CF_3)_2C{=}CF_2 \xrightarrow{H_2O} (CF_3)_2CHCOOH \xrightarrow{P_2O_5} \underset{(VII)}{(CF_3)_2C{=}C{=}O} \xrightarrow[\text{catalyst}]{t^\circ} \to \underset{\displaystyle CF_3}{\underset{|}{CF_2{=}C}}{-}COF \quad (I) \quad .$$

This reaction takes place when gaseous bis(trifluoromethyl)keten is passed over NaF at 200–300°C[2-5] or through a hollow glass tube at 400°C[6] and also on heating under pressure with glass wool[1], with a catalytic amount of $Et_2O.BF_3$,[7] or with butylether (preferably in the presence of $ZnCl_2$).[1]

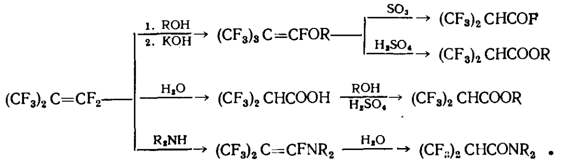
The reaction is reversible; resulting in the formation of equilibrium mixtures containing about 60% of bis(trifluoromethyl)keten (b.p. 5–6°C) and about 40% of perfluoromethacryloyl fluoride (b.p. 51.5°C). The catalytic effect of NaF indicates the intermediate formation of a mesomeric fluorine-containing carbanion (A); in the absence of NaF, small amounts of F^- ions are obtained, probably as a result of the etching of the glass[6]. On the other hand, in the isomerisation under the influence of Lewis acids ($ZnCl_2$ and BF_3), the elimination of the F^- anion with intermediate formation of a mesomeric carbonium ion (B) is postulated[7]:



The isomerisation of bis(trifluoromethyl)keten is the most convenient method for the preparation of perfluoromethacryloyl fluoride. However, unfortunately other PFMA derivatives cannot usually be obtained directly from the acid fluoride, since attack by nucleophiles is directed primarily to the β-carbon atom of the "acrylic" system and not to the carbonyl group (see Section **III**). The formation of **PFMA** derivatives from the fluoride (**I**) therefore requires protection of the reactive $CF_2{=}C<$ group (for example by halogenation) followed by reaction with a nucleophile (e.g. an alcohol), and the removal of the protecting group[8]†. Incidentally, in most cases it is more convenient to use other methods for the synthesis of PFMA derivatives—dehydrofluorination of derivatives of α-hydrohexafluoroisobutyric acid and electrophilic elimination of alkyl fluorides from alkoxypolyfluoroisobutenes.

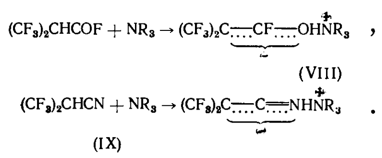
2. Dehydrofluorination of α-Hydrohexafluoroisobutyric Acid Derivatives

Derivatives of α-hydrohexafluoroisobutyric acid (HFIBA) are fairly readily available; they are obtained from perfluoroisobutene (see, for example, Refs. 9–11):



These derivatives contain in the α-position a labile hydrogen atom and in principle should be readily dehydrofluorinated in the presence of bases. However, the usual methods for the preparation of perfluoro-olefins—dehydrofluorination of fluoroalkanes by alkalis[12–14]—is inapplicable in this instance, since PFMA derivatives very readily undergo further attack by the nucleophiles[7] (see Section III).

When the acid fluoride of HFIBA is acted upon by triethylamine, only the first dehydrofluorination stage is achieved—the elimination of the proton—and the stable salt (VIII), containing the mesomeric perfluoroisobutenoxide anion, is formed[1]. The nitrile of HFIBA (IX) reacts similarly[15]:



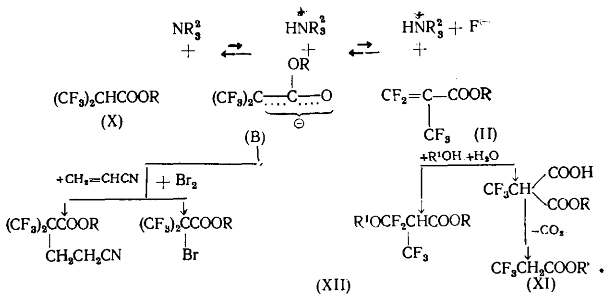
$$(CF_3)_2CHCOF + NR_3 \rightarrow (CF_3)_2C\underbrace{\cdots CF\cdots}_{-}O\overset{+}{H}NR_3 \text{ ,}$$

(VIII)

$$(CF_3)_2CHCN + NR_3 \rightarrow (CF_3)_2C\underbrace{\cdots C\cdots}_{-}N\overset{+}{H}NR_3 \text{ .}$$

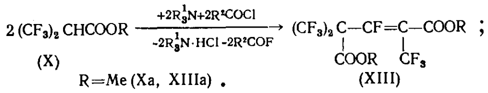
(IX)

HFIBA esters (X) in which the hydrogen atom is less mobile, form on treatment with a tertiary amine equilibrium mixtures containing mainly the initial ester together with small amounts of the mesomeric carbanion (C) and PFMA esters (II). The addition of a third component, which reacts either with the carbanion or with the PFMA ester, displaces the equilibrium towards the formation of the final products[6,14]. Indeed, in the presence of triethylamine or pyridine, HFIBA esters are readily brominated[16,17] and cyanoethylated[18] and, on treatment with water and alcohols, give respectively the esters of βββ-trifluoropropionic acid (XI)[19] and those of α-hydro-β-alkoxypentafluoroisobutyric acids (XII)[20]:



(1)

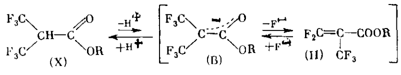
The removal of the F⁻ anion from the equilibrium (for example on treatment with an acyl chloride) should lead to the formation of the PFMA ester. It is known that, when nonafluoroisobutane $(CF_3)_3CH$ reacts with triethylamine and benzoyl chloride it is dehydrofluorinated, yielding perfluoroisobutene $(CF_3)_2C{=}CF_2$.[20] However, the analogous reaction with the HFIBA ester leads only to the "dimer" (XIIIa):[21,22]



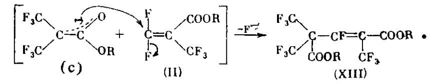
$$2(CF_3)_2CHCOOR \xrightarrow[-2R_3^1N\cdot HCl-2R^2COF]{+2R_3^1N+2R^2COCl} (CF_3)_2\underset{COOR}{C}{-}CF{=}\underset{CF_3}{C}{-}COOR \text{ ;}$$

(X) R=Me (Xa, XIIIa) . (XIII)

Evidently this involves the intermediate formation of the PFMA ester (II), but the exceptional reactivity of this compound precludes its isolation, since it reacts immediately with the fluoro-carbanion (C); substitution of the vinyl fluorine atom yields the "dimer" (XIII):



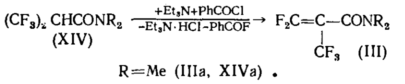
(2)



(3)

The analogous interaction of triethylammonium perfluoroisobutenoxide (VIII) with an acyl chloride leads to "δ-lactone-dimers"[6,23] [cf. Eqn. (10)].

The dimethylamide of PFMA, which is less reactive than its fluoride and esters, can be obtained from the saturated amide (XIVa) on treatment with triethylamine and benzoyl chloride[7]:

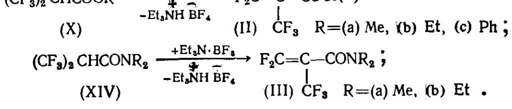


$$(CF_3)_2CHCONR_2 \xrightarrow[-Et_3N\cdot HCl-PhCOF]{+Et_3N+PhCOCl} F_2C{=}\underset{CF_3}{C}{-}CONR_2 \text{ ;}$$

(XIV) (III)

R=Me (IIIa, XIVa) .

A very convenient dehydrofluorinating agent for the synthesis of PFMA derivatives from the corresponding HFIBA derivatives proved to be the adduct of triethylamine with boron trifluoride $Et_3N.BF_3$. On treatment with this adduct, the esters and dialkylamides of HFIBA are converted into the PFMA derivatives (II) and (III) in high yields[7,10,24]:



$$(CF_3)_2CHCOOR \xrightarrow[-Et_3\overset{+}{N}H\,\overset{-}{B}F_4]{+Et_3N\cdot BF_3} F_2C{=}\underset{CF_3}{C}{-}COOR \text{ ;}$$

(X) (II) R=(a) Me, (b) Et, (c) Ph ;

$$(CF_3)_2CHCONR_2 \xrightarrow[-Et_3\overset{+}{N}H\,\overset{-}{B}F_4]{+Et_3N\cdot BF_3} F_2C{=}\underset{CF_3}{C}{-}CONR_2 \text{ ;}$$

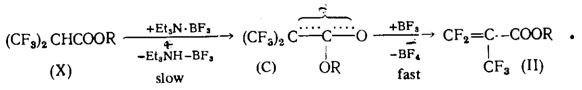
(XIV) (III) R=(a) Me, (b) Et .

---

† The method for the preparation of methyl perfluoromethacrylate from the acid fluoride via perfluoromethacryloyl fluorosulphonate (V) is described at the end of Section II.

‡ The ester of difluoromethylenemalonic acid $F_2C{=}C(COOMe)_2$ has been obtained similarly from the ester of trifluoromethylmalonic acid[25].

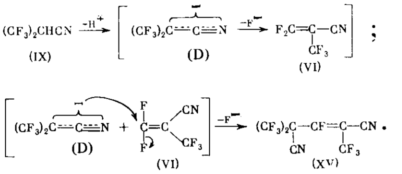
There are no "dimers" in the reaction products even when HFIBA esters are dehydrofluorinated. Evidently the nucleophilic properties of the adduct $Et_3N.BF_3$ are reduced so much that the carbanion (C) is formed slowly compared with the next stage—the elimination of the F^- anion from the carbanion:



$$\underset{(X)}{(CF_3)_2CHCOOR} \xrightarrow[\substack{-Et_3\overset{+}{N}H-BF_3 \\ \text{slow}}]{+Et_3N\cdot BF_3} \underset{(C)}{(CF_3)_2C\cdots\underset{OR}{C}\cdots O^-} \xrightarrow[\substack{-\overset{-}{BF_4} \\ \text{fast}}]{+BF_3} \underset{CF_3\ (II)}{CF_2{=}C{-}COOR} \ .$$

The carbanion (C) does not accumulate in the mixture and there is not sufficient time for its reaction with the PFMA ester, which would lead to the "dimer" (XIII). The dehydrofluorination of the dimethylamide of PFMA is accelerated in the presence of triethylamine and retarded in the presence of $Et_2O.BF_3$. This apparently confirms that the slowest stage determining the rate of the entire dehydrofluorination process is heterolysis of the C–H bond[10].

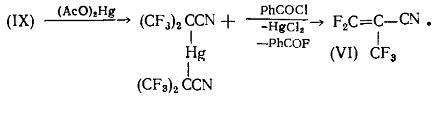
When an attempt was made to synthesise perfluoromethacrylonitrile by this procedure from the nitrile of HFIBA, only the "dimer" (XV) was obtained. The equilibrium in the heterolysis of the C–H bond of a strong CH acid such as the nitrile (IX) is displaced to the right[15], so that sufficient carbanion (D) is obtained for it to be able to react with perfluoromethacrylonitrile, forming the dinitrile (XV)[10]:



(4)

When the less basic adduct of pyridine and boron trifluoride was used, only the "dimer" was again obtained[10].

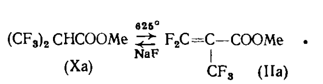
Perfluoromethacrylonitrile can be synthesised from the saturated nitrile (IX) by an indirect procedure—via an organomercury derivative[26]:



$$(IX) \xrightarrow{(AcO)_2Hg} \underset{\substack{| \\ Hg \\ | \\ (CF_3)_2CCN}}{(CF_3)_2CCN} + \xrightarrow[\substack{-HgCl_2 \\ -PhCOF}]{PhCOCl} \underset{(VI)\ CF_3}{F_2C{=}C{-}CN} \ . \qquad (5)$$

Yet another method for the synthesis of PFMA derivatives from the corresponding HFIBA derivatives involves thermal dehydrofluorination in the vapour phase over a catalyst. In the dehydrofluorination of the fluoride of HFIBA, the reaction is complicated by isomerisation and dimerisation. Thus, when the vapour of the HFIBA fluoride was passed over NaF, a mixture of perfluoromethacryloyl fluoride and bis(trifluoromethyl)keten was obtained[9]. Under other conditions, treatment with KF leads to the formation of "δ-lactone-dimers" [cf. Eqn. (10)] and at 400°C over glass wool one obtains a mixture containing 1,1,3,3,3-pentafluoropropene and other products in addition to perfluoromethacryloyl fluoride and bis(trifluoromethyl)keten[8].

Methyl perfluoromethacrylate is obtained by the dehydrofluorination of the methyl ester of HFIBA over sodium chloride[9,27]:

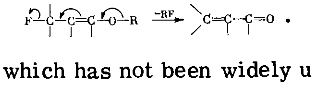


$$\underset{(Xa)}{(CF_3)_2CHCOOMe} \underset{NaF}{\overset{625^\circ}{\rightleftarrows}} \underset{CF_3\quad (IIa)}{F_2C{=}C{-}COOMe} \ . \qquad (6)$$

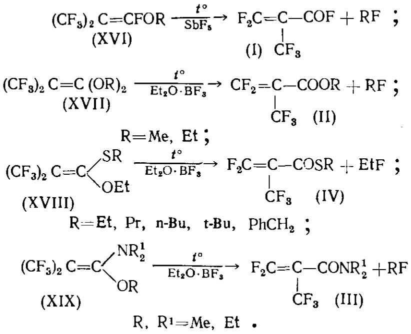
This results in the formation of an equilibrium mixture containing almost equal amounts of the dehydrofluorination products and of the initial saturated ester; the separation of the mixture by distillation is difficult owing to the similar boiling points of these two compounds. It has been stated (without experimental evidence) that it is useful to employ NaF together with quartz in this reaction[27] §.

3. Electrophilic Elimination of Alkyl Fluorides from Alkoxypolyfluoroisobutenes

One of the possible ways of forming a fluorine-containing conjugated αβ-unsaturated carbonyl system involves the elimination of an alkyl fluoride from an alkoxyfluoroolefin[29–31]:



This method, which has not been widely used in other instances, has been successfully employed to synthesise PFMA derivatives from the relatively readily available alkoxypolyfluoroisobutenes[7,32–34]. Thus, when alkyl perfluoroisobutenyl ethers (XVI) are heated in the presence of catalytic amounts of SbF_5 or $Et_2O.BF_3$ with simultaneous distillation of the product, perfluoromethacryloyl fluoride is formed[33]. On heating dialkylacetals of bis(trifluoromethyl)keten (XVII), dialkylthioacetals (XVIII), or *ONN*-trialkylaminoacetals (XIX) with a catalytic amount of $Et_2O.BF_3$, the corresponding esters[33], thiolo-esters[34], or dialkylamides of PFMA are formed[33]¶.



$$\underset{(XVI)}{(CF_3)_2C{=}CFOR} \xrightarrow[SbF_5]{t^\circ} \underset{(I)\ CF_3}{F_2C{=}C{-}COF} + RF \ ;$$

$$\underset{(XVII)}{(CF_3)_2C{=}C(OR)_2} \xrightarrow[Et_2O\cdot BF_3]{t^\circ} \underset{CF_3\quad (II)}{CF_2{=}C{-}COOR} + RF \ ;$$

R=Me, Et ;

$$\underset{(XVIII)}{(CF_3)_2C{=}C\begin{matrix} SR \\ OEt \end{matrix}} \xrightarrow[Et_2O\cdot BF_3]{t^\circ} \underset{CF_3\quad (IV)}{F_2C{=}C{-}COSR} + EtF \ ;$$

R=Et, Pr, n-Bu, t-Bu, $PhCH_2$;

$$\underset{(XIX)}{(CF_3)_2C{=}C\begin{matrix} NR^1_2 \\ OR \end{matrix}} \xrightarrow[Et_2O\cdot BF_3]{t^\circ} \underset{CF_3\quad (III)}{F_2C{=}C{-}CONR^1_2} + RF \ ;$$

R, R^1=Me, Et .

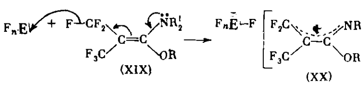
These reactions are carried out at approximately 100–140°C. Ethyl fluoride is usually split off under somewhat milder conditions than methyl fluoride[7,33]. On heating to 200°C, the aminoacetal (XIX, R = R^1 = Me) is cleaved even in the absence of a catalyst. The role of the Lewis acid evidently involves the elimination of the allyl fluorine atom from the alkoxyolefin, which leads to the formation of a mesomeric carbonium ion. Stable salts (XX) containing

---

§ In the dehydrofluorination of 2,3,3,3-tetrafluoropropionyl fluoride, the use of NaF and quartz makes it possible to obtain perfluoroacryloyl fluoride in a high yield. The tube is packed alternately with these two catalysts, which are arranged in layers[28].

¶ Perfluoroacryloyl fluoride has been obtained similarly from the esters $CF_3CF{=}CFOR$[7,33], and the esters of difluoromethylenemalonic acid $CF_2{=}C(COOR)COOR^1$ have been synthesised from the acetals of alkoxycarbonyltrifluoromethylketens[35].

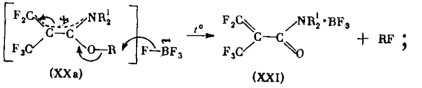
such cations have been obtained from the aminoacetals (XIX)[7,33]:



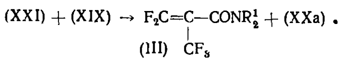
$F_nE = BF_3$ (a), SbF_5 .

The cleavage of aminoacetals on heating with catalytic amounts of a Lewis acid is carried out in accordance with the following scheme (each stage has been confirmed experimentally): the formation of a salt (XXa) [Eqn. (7)]; the cleavage of this salt on heating owing to the alkylation of the complex anion BF_4^- by the mesomeric carbonium ion [Eqn. (8)]; the exchange reaction between the adduct of the dialkylamide of PFMA with boron trifluoride (XXI), on the one hand, and the next aminoacetal molecule, on the other, which results in the formation of the final product—the dialkylamide of PFMA (III)—and the regeneration of the salt (XXa) [Eqn. (9)]; the salt is again cleaved and this is continued until almost the entire aminoacetal is converted into the alkyl fluoride and the dialkylamide of PFMA[7,33]:

$$(XIX) + Et_2O \cdot BF_3 \rightarrow (XXa) + Et_2O \ ; \qquad (7)$$



(8)

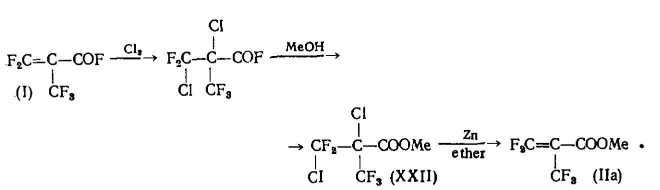


$$(XXI) + (XIX) \rightarrow \underset{(III)}{F_2C{=}\underset{CF_3}{C}{-}CONR'_2} + (XXa) \ . \qquad (9)$$

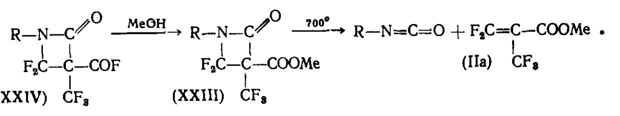
The mechanism of the cleavage of the esters (XVI), the acetals (XVII), and the thioacetals (XVIII) probably differs in detail from the above scheme, but the role of the Lewis acid as an agent for the elimination of the F⁻ ion remains[7].

4. Other Methods for the Synthesis of PFMA Derivatives

A PFMA ester was obtained for the first time by the dechlorination of an ester of $\alpha\beta$-dichloropentafluoroisobutyric acid (XXII)[8]:

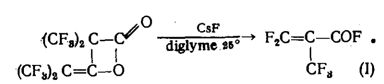


The same ester is formed in a low yield on thermal cleavage of 2-oxoacetidine-3-carboxylic acid ester (XXIII) obtained from the 1,2-cycloadduct of perfluoromethacryloyl fluoride with alkyl isocyanate (XXIV)[5,36] (see subsection 7 in this Section):



A new method for synthesising a PFMA ester, involving the interaction of perfluoromethacryloyl fluorosulphonate (V) with methyl ether[37] [see Eqn. (15)], has been proposed recently. A disadvantage of this method is the difficulty of separating the mixture containing the PFMA ester and FSO_3Me. The mixed anhydride (V) was obtained by treating perfluoromethacryloyl fluoride with SO_3 [see Eqn. (22)].

Perfluoromethacryloyl fluoride is formed in a low yield together with other products when the "β-lactone-dimer of bis(trifluoromethyl)keten" is treated with CsF[3]:

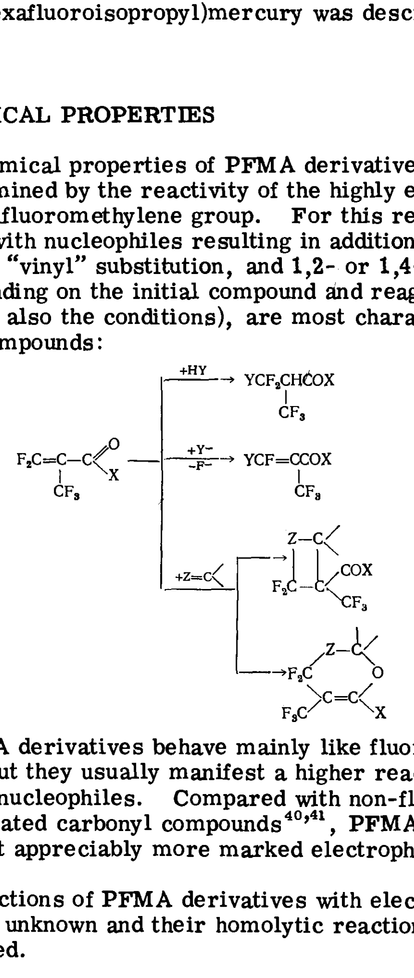


The mechanism of this reaction is obscure. Possibly the dimer decomposes at least partially with formation of bis(trifluoromethyl)keten, which isomerises to perfluoromethacryloyl fluoride.

The formation of perfluoromethacrylonitrile from bis(α-cyanohexafluoroisopropyl)mercury was described above [Eqn. (5)].

III. CHEMICAL PROPERTIES

The chemical properties of PFMA derivatives are as a rule determined by the reactivity of the highly electrophilic terminal difluoromethylene group. For this reason, reactions with nucleophiles resulting in addition to the C=C bond, "vinyl" substitution, and 1,2- or 1,4-cycloaddition, depending on the initial compound and reagents (and sometimes also the conditions), are most characteristic of these compounds:

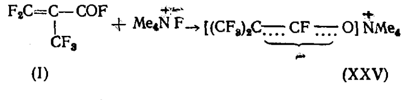


Thus PFMA derivatives behave mainly like fluoro-olefins[38,39], but they usually manifest a higher reactivity with respect to nucleophiles. Compared with non-fluorinated $\alpha\beta$-unsaturated carbonyl compounds[40,41], PFMA derivatives also exhibit appreciably more marked electrophilic properties.

The reactions of PFMA derivatives with electrophiles are almost unknown and their homolytic reactions have been little studied.

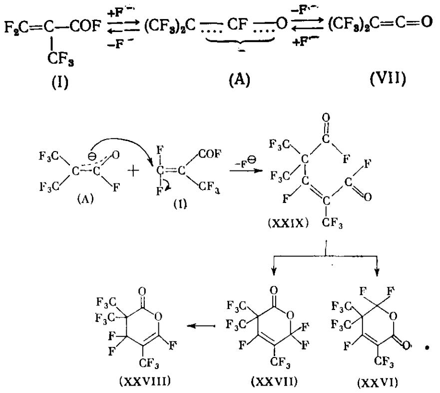
1. Reactions with Halide Anions

Perfluoromethacryloyl fluoride reacts readily with the F⁻ anion, forming a mesomeric fluoro-carbanion—the perfluoroisobutenoxide anion (A).[6] Depending on the reaction conditions, the subsequent fate of this carbanion may be various. Thus, when perfluoromethacryloyl fluoride reacts with tetramethylammonium fluoride in acetonitrile, the tetramethylammonium salt (XXV) is formed[42]:



On heating at 300°C over NaF, perfluoromethacryloyl fluoride reversibly isomerises to bis(trifluoromethyl)keten[2-5] (see subsection 1 of Section II).

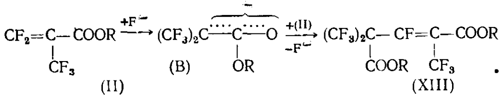
When perfluoromethacryloyl fluoride or the isomeric bis(trifluoromethyl)keten are acted upon by alkali metal fluorides or triethylamine, the "δ-lactone-dimers" (XXVI), (XXVII), and (XXVIII) are formed[3,21,43]. Evidently, the initial product is the mesomeric carbanion (A), which reacts with perfluoromethacryloyl fluoride, substituting the vinyl fluorine atoms, and the resulting dicarboxylic acid fluoride (XXIX) cyclises to the "δ-lactone-dimers" (XXVI) and (XXVII); the isomerisation of compound (XXVII) leads to compound (XXVIII):[6]



(10)

The dimerisation to "δ-lactone-dimers" also occurs in the presence of tetraethylammonium chloride[3,44] or zinc chloride[45].

PFMA esters dimerise very readily in the presence of the F^- ion, forming the dicarboxylic acid esters (XIII)[10,46,47]† [see also Eqns. (3), (14), and (21)]:



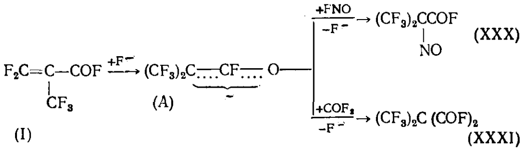
$$\underset{\text{(II)}}{\mathrm{CF_2{=}\underset{\displaystyle CF_3}{C}{-}COOR}} \xrightarrow{+F^-} \underset{\text{(B)}}{\mathrm{(CF_3)_2C\overset{\cdots}{-}\underset{\displaystyle OR}{C}\overset{\cdots}{-}O^-}} \xrightarrow[-F^-]{+(II)} \underset{\text{(XIII)}}{\mathrm{(CF_3)_2\underset{\displaystyle COOR}{C}{-}CF{=}\underset{\displaystyle CF_3}{C}{-}COOR}} .$$

Perfluoromethacrylonitrile dimerises even more readily and cannot be obtained even in the presence of the adduct $R_3N.BF_3$ [10] [see Eqn. (4)]. The less reactive dialkyl amides of PFMA show no tendency towards dimerisation[7,46].

The perfluoro-t-butyl anion $(CF_3)_3C^-$, formed when the F^- ion adds to perfluoroisobutene, reacts with a wide variety of electrophiles, yielding the compounds $(CF_3)_3CR$. [49-52] The mesomeric carbanions obtained from PFMA derivatives and the F^- anion are also capable of combining with electrophiles, although such reactions have been studied much less than in the case of perfluoroisobutene.

The addition of a proton results in the formation of HFIBA derivatives. Thus methyl perfluoromethacrylate combines with hydrogen fluoride in the presence of NaF, the reaction being reversible[9,27]‡ [Eqn. (6)]. Like perfluoroisobutene[53,54], PFMA esters can play the role of dehydrofluorinating agents in the presence of tertiary amines [Eqn. (19)]. The dimethylamide of PFMA reacts with hydrogen fluoride evolved when the vinyl fluorine atom is substituted on treatment with phenols or mercaptans [Eqns. (13) and (18)].

The interaction of nitrosyl fluoride with perfluoromethacryloyl fluoride, leading to the fluoride of the α-nitrosocarboxylic acid (XXX), probably also begins with the addition of the F^- anion to the C=C bond[55] (cf. Ref. 38). On treatment with carbonyl difluoride in the presence of KF, perfluoromethacryloyl fluoride is converted into the difluoride of bis(trifluoromethyl)malonic acid (XXXI):[56]§

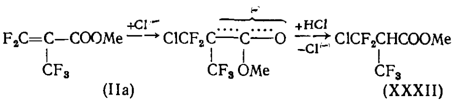


$$\underset{\text{(I)}}{\mathrm{F_2C{=}\underset{\displaystyle CF_3}{C}{-}COF}} \xrightarrow{+F^-} \underset{(A)}{\mathrm{(CF_3)_2C\overset{\cdots}{-}CF\overset{\cdots}{-}O^-}} \xrightarrow[-F^-]{+FNO} \underset{\text{(XXX)}}{\mathrm{(CF_3)_2\underset{\displaystyle NO}{C}COF}}$$

$$\mathrm{(CF_3)_2C\overset{\cdots}{-}CF\overset{\cdots}{-}O^-} \xrightarrow[-F^-]{+COF_2} \underset{\text{(XXXI)}}{\mathrm{(CF_3)_2C(COF)_2}} .$$

(11)

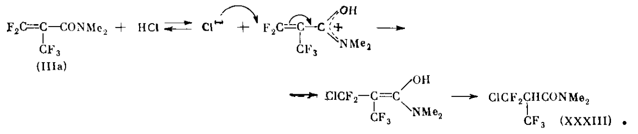
Methyl perfluoromethacrylate does not react with hydrogen chloride at room temperature in the absence of a catalyst, but, in the presence of a catalytic amount of pyridinium chloride, it readily gives rise to the chloropentafluoroisobutyrate ester (XXXII)[57]¶:



$$\underset{\text{(IIa)}}{\mathrm{F_2C{=}\underset{\displaystyle CF_3}{C}{-}COOMe}} \xrightarrow{+Cl^-} \mathrm{ClCF_2\underset{\displaystyle CF_3}{C}\overset{\cdots}{-}\underset{\displaystyle OMe}{C}\overset{\cdots}{-}O^-} \xrightarrow[-Cl^-]{+HCl} \underset{\text{(XXXII)}}{\mathrm{ClCF_2\underset{\displaystyle CF_3}{C}HCOOMe}} .$$

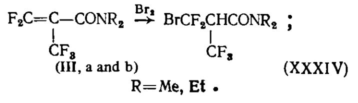
In the absence of a catalyst, perfluoromethacrylonitrile does not react with hydrogen chloride and bromide even at 150°C.[26]

In contrast to the ester and the nitrile, the dimethylamide of PFMA readily combines with hydrogen chloride in a non-polar solvent in the absence of a catalyst, forming the amide of the chloro-substituted acid (XXXIII).[57] Evidently we are dealing here with "intramolecular base catalysis". The protonation of the amide group leads, on the one hand, to the activation of the PFMA dialkylamide molecule, and, on the other, to the appearance in the mixture of the fairly nucleophilic anion Cl^-, which is capable of attacking the β-carbon atom[46,57]:



$$\mathrm{F_2C{=}\underset{\displaystyle CF_3}{C}{-}CONMe_2} + \mathrm{HCl} \rightleftarrows \mathrm{Cl^-} + \mathrm{F_2C{=}\underset{\displaystyle CF_3}{C}{-}C(OH)(NMe_2)^+} \longrightarrow \mathrm{ClCF_2{-}\underset{\displaystyle CF_3}{C}{=}C(OH)(NMe_2)} \longrightarrow \mathrm{ClCF_2\underset{\displaystyle CF_3}{C}HCONMe_2} .$$

The hydrogen bromide addition products (XXXIV) have been obtained in low yields in attempts to brominate PFMA dialkylamides[7]:



$$\underset{\text{(III, a and b)}}{\mathrm{F_2C{=}\underset{\displaystyle CF_3}{C}{-}CONR_2}} \xrightarrow{Br_2} \underset{\text{(XXXIV)}}{\mathrm{BrCF_2\underset{\displaystyle CF_3}{C}HCONR_2}} ;$$

$$\mathrm{R{=}Me, Et} .$$

(12)

[†] The esters of difluoromethylenemalonic acid dimerise just as readily[21,35]. The analogous dimerisation of perfluoroisobutene[48] and the perfluoroacrylate ester[9] has also been described.

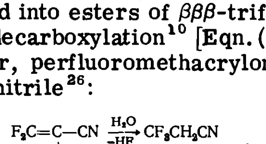
[‡] Perfluoroacryloyl fluoride also combines with HF in the presence of NaF.[9]

[§] Perfluoroacryloyl fluoride gives rise similarly to the difluoride of α-fluoro-α-trifluoromethylmalonic acid[56]. The analogous reaction with a perfluoromethacrylate ester is described in subsection 7 of the present Section.

[¶] Perfluoroisobutene also combines with hydrogen halides in the presence of bases[58].

2. Reactions with *O*-Nucleophiles

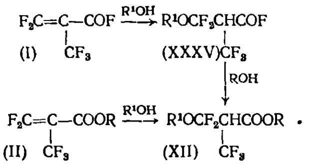
Perfluoromethacryloyl fluoride reacts readily with water, being converted into trifluoromethylmalonic acid $CF_3CH(COOH)_2$.[7] When HFIBA esters react with water in the presence of triethylamine, the intermediate PFMA esters are converted into esters of $\beta\beta\beta$-trifluoropropionic acid as a result of decarboxylation[10] [Eqn. (1)]. On treatment with water, perfluoromethacrylonitrile yields $\beta\beta\beta$-trifluoropropionitrile[26]:



$$\underset{CF_3}{F_2C{=}\overset{}{C}{-}CN} \xrightarrow[-HF,\ -CO_2]{H_2O} CF_3CH_2CN \ .$$

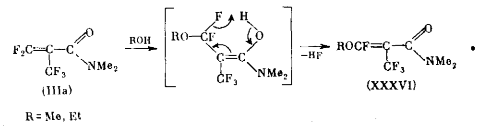
(VI)

The C=C double bond in perfluoromethacryloyl fluoride is so electrophilic that it reacts with hydroxy-compounds faster than the acid fluoride group. On treatment with equimolar amounts of alcohols ($MeOH$, $CH_2{=}CHCH_2OH$, $HOCH_2COOMe$) under mild conditions, perfluoromethacryloyl fluoride is converted into the corresponding addition products (XXXV)[9,27] [see also Eqn. (17)]†. The COF group also reacts with an excess of the alcohol, forming esters of α-hydro-β-alkoxypentafluoroisobutyric acids (XII)[4,8,21,59]. PFMA esters likewise combine readily with alcohols, forming the adducts (XII)[8,59]‡:



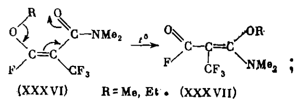
$$\begin{array}{ccc} \underset{(I)\quad CF_3}{F_2C{=}C{-}COF} & \xrightarrow{R^1OH} & \underset{(XXXV)\,CF_3}{R^1OCF_2CHCOF} \\ & & \downarrow{\scriptstyle ROH} \\ \underset{(II)\quad CF_3}{F_2C{=}C{-}COOR} & \xrightarrow{R^1OH} & \underset{(XII)\quad CF_3}{R^1OCF_2CHCOOR} \ . \end{array}$$

In contrast to the acid fluoride and esters, the dimethylamide of PFMA reacts with alcohols to form only products arising from the substitution of the vinyl fluorine atom—the dimethylamides of β-alkoxy-β-fluoro-α-trifluoromethylacrylic acids (XXXVI) (in the form of a mixture of *cis*- and *trans*-isomers)[59]§. This difference can probably be accounted for by the appreciable basicity of the $CONMe_2$ group, which can bind the proton and can prevent its addition to the carbanionic centre[7,46,59]:

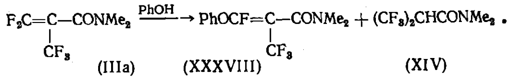


Perfluoroisobutene is known to react readily with alcohol, forming mainly addition products together with small amounts of substitution products[61,62]. It has been shown by the method of competition kinetics that methyl perfluoromethacrylate reacts with alcohol much faster than perfluoroisobutene or PFMA dimethylamide[46].

The β-alkoxyamides (XXXVI) have proved to be relatively unstable. They rearrange on heating to the acid fluorides (XXXVII) as a result of the 1,5-migration of the alkyl group from the "enolic" oxygen atom to the carbonyl oxygen atom of the alkoxyvinylcarbonyl system[59]:

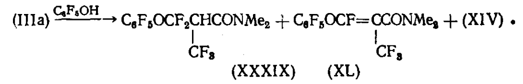


In contrast to the reaction with alcohols, in the reaction with phenols the PFMA ester is less reactive than PFMA dimethylamide. Methyl perfluoromethacrylate does not react with phenol and pentafluorophenol at room temperature¶, while PFMA dimethylamide does react under these conditions, although more slowly than in the analogous reaction with alcohols[57]. The reaction with unsubstituted phenol yields the "vinyl" substitution product (XXXVIII) (the *cis*- and *trans*-isomers); the hydrogen fluoride evolved adds to the initial amide (IIIa), forming the dimethylamide of HFIBA (XIV):



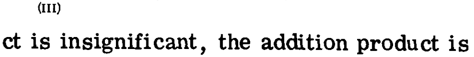
$$\underset{(IIIa)}{\underset{CF_3}{F_2C{=}C{-}CONMe_2}} \xrightarrow{PhOH} \underset{(XXXVIII)}{\underset{CF_3}{PhOCF{=}C{-}CONMe_2}} + \underset{(XIV)}{(CF_3)_2CHCONMe_2} \ . \qquad (13)$$

Pentafluorophenol forms mainly the addition product (XXXIX) and only small amounts of the substitution product (XL) (the *cis*- and *trans*-isomers):



$$(IIIa) \xrightarrow{C_6F_5OH} \underset{(XXXIX)}{\underset{CF_3}{C_6F_5OCF_2CHCONMe_2}} + \underset{(XL)}{\underset{CF_3}{C_6F_5OCF{=}CCONMe_2}} + (XIV) \ .$$

Comparison of the reactivities of various *O*- and *S*-nucleophiles in reactions with PFMA dimethylamide showed that the rate of reaction decreases in a sequence which is quite different from the sequence of the corresponding acidities: AlkOH ($pK_a \simeq 18$) > RCOOH† ($pK_a = 0.23$–4.75) > PhSH‡ ($pK_a = 8.0$) > C_6F_5OH ($pK_a = 5.5$) > $PhCH_2SH$‡ ($pK_a \simeq 12$) > PhOH ($pK_a = 9.9$) ≫ $(CF_3)_2CHOH$ ($pK_a = 9.3$). Evidently, when the nature of the nucleophile (acidity, nucleophilic properties of the reaction centre) changes appreciably, there is also a change in reaction mechanism, the influence of the basic properties of the amide group having an effect to different extents[46,57]. The $+M$ effect of the substituent X, which promotes the dissociation of the C−F bond, probably plays a significant role in the formation of the "vinyl" substitution products:



If this effect is insignificant, the addition product is formed in a larger amount as a result of the attack by the proton on the central carbon atom.

Little information is available about the interaction of PFMA derivatives with alkoxides and phenoxides. The reaction of perfluoromethacryloyl fluoride with sodium methoxide followed by hydrolysis yields the ester of trifluoromethylmalonic acid (XLI).[9] This probably involves

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†The analogous reaction of perfluoroacryloyl fluoride with methanol takes place in the presence of NaF and leads to a mixture containing $MeOCF_2CHFCOOMe$ and $MeOCF_2CHFCOF$ as well as traces of $F_2C{=}CFCOOMe$ and $CF_3CHFCOOMe$.[9]

‡It has been stated[26] that perfluoromethacrylonitrile reacts very readily with alcohols, but the structure of the resulting products has not been given. Ethyl perfluoroacrylate reacts with alcohols under somewhat more severe conditions[60].

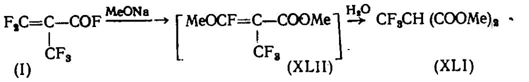
§Hexafluoroisopropyl alcohol $(CF_3)_2CHOH$ does not react with PFMA dimethylamide at room temperature[57].

¶ Perfluoromethacryloyl fluoride reacts with phenol at 100°C to form the adduct $PhOCF_2CH(CF_3)COF$.[9]

†See Eqn. (16).

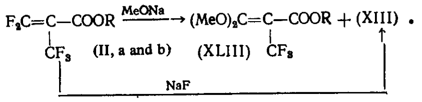
‡See Eqn. (18).

the initial formation of the "vinyl" substitution product (**XLII**):



$$\underset{(I)}{F_2C{=}\underset{CF_3}{\underset{|}{C}}{-}COF} \xrightarrow{MeONa} \left[MeOCF{=}\underset{CF_3}{\underset{|}{C}}{-}COOMe\right]_{(XLII)} \xrightarrow{H_2O} \underset{(XLI)}{CF_3CH(COOMe)_2}$$

Treatment of **PFMA** esters with sodium methoxide leads to the formation of acetals of the substituted ketens (**XLIII**) together with the "dimers" (**XIII**):[47]



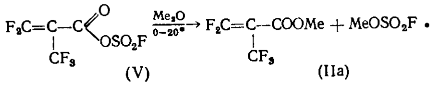
$$F_2C{=}\underset{CF_3}{\underset{|}{C}}{-}COOR \xrightarrow{MeONa} (MeO)_2C{=}\underset{CF_3}{\underset{|}{C}}{-}COOR + (XIII)$$

(II, a and b) (XLIII) NaF

(14)

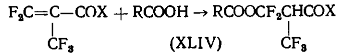
The "vinyl" substitution product (**XXXVIII**) has been obtained from PFMA dimethylamide and sodium phenoxide[57].

The mixed anhydride of **PFMA** and fluorosulphonic acid (**V**) readily reacts with methyl ether. In contrast to other reactions of **PFMA** derivatives with nucleophiles, the β-carbon atom is not involved in this process and one **PFMA** derivative is thus converted into another; this results in the formation of a **PFMA** ester and methyl fluorosulphonate[37]:



(V) (IIa) (15)

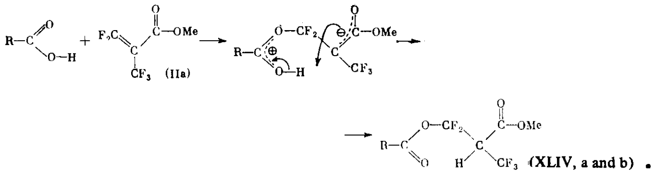
PFMA derivatives are able to combine even with very slightly nucleophilic carboxylic acids in the absence of basic catalysts. Methyl perfluoromethacrylate reacts readily with acetic or trifluoroacetic acid, forming the addition products (**XLIV**, a and b). The analogous reactions of **PFMA** dimethylamide led to the β-acyloxyamides (**XLIV**, c, d, and e):[57]



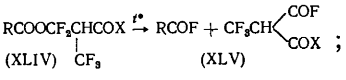
$$\underset{(IIa),\ (IIIa)}{F_2C{=}\underset{CF_3}{\underset{|}{C}}{-}COX} + RCOOH \rightarrow \underset{(XLIV)}{RCOOCF_2\underset{CF_3}{\underset{|}{C}}HCOX} \qquad (16)$$

(a) $X{=}OMe,\ R{=}Me;$
(b) $X{=}OMe,\ R{=}CF_3;$
(c) $X{=}NMe_2,\ R{=}Me;$
(d) $X{=}NMe_2,\ R{=}CF_3;$
(e) $X{=}NMe_2,\ R{=}Ph.$

Whereas "intramolecular base catalysis" can be suggested for the reactions with **PFMA** dimethylamide, this is much less likely for the **PFMA** ester (see subsection 1 in this Section); possibly the carboxylic acid, even trifluoroacetic acid, behaves as a nucleophile in the reaction with the **PFMA** ester[57]. The addition probably takes place via a six-membered cyclic transition state, which facilitates the reaction[46]:

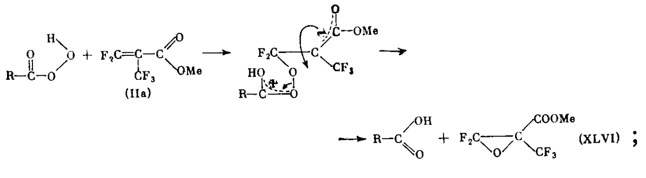


The addition of carboxylic acids is not characteristic of the usual $\alpha\beta$-unsaturated carbonyl compounds[41]. This can also be said of electrophilic perfluoro-olefins. Only in the presence of a base (triethylamine) does perfluoroisobutene react with acetic acid, but the resulting adduct immediately decomposes into acetyl fluoride and the fluoride of HFIBA.[23] The analogous cleavage of the adduct (**XLIV**) takes place on heating and leads to derivatives of trifluoromethylmalonic acid (**XLV**) containing one acyl fluoride group[57]:



$R{=}Me,\ CF_3;\ X{=}OMe,\ NMe_2.$

Peracids are probably more powerful nucleophiles than carboxylic acids[63]. It is therefore not surprising that peracids react still faster with the **PFMA** ester. However, they give rise to an epoxide [the fluorine-containing glycidyl ether (**XLVI**)] in this reaction and not to addition products[46,64]:

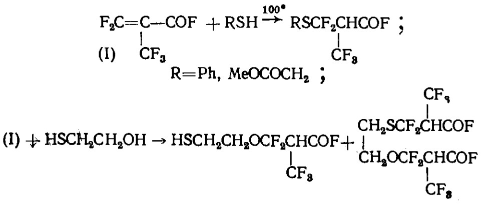


$R = Ph,\ p\text{-}O_2NC_6H_4,\ m\text{-}ClC_6H_4.$

In the usual epoxidation of ethylenic compounds by peracids (the Prilezhaev reaction), the latter are known to behave as electrophiles and the introduction of electron-withdrawing substituents into the molecule of the unsaturated compound hinders its epoxidation[63]. However, it has been found that the **PFMA** ester is epoxidised more readily than perfluoroisobutene or methyl acrylate[64]. Evidently the epoxidation of the highly electrophilic **PFMA** ester involves an unusual inversion of the mechanism of the Prilezhaev reaction, the peracid behaving as a nucleophile. O-Nucleophiles capable of reacting with **PFMA** derivatives include also certain carbonyl compounds. Reactions with these compounds, leading to cycloadducts or their conversion products, are examined in a separate subsection (subsection 7).

3. Reactions with *S*-Nucleophiles

The reactions of **PFMA** derivatives with mercapto-compounds have been little investigated. Perfluoromethacryloyl fluoride gives rise to products formed by addition to the C=C bond on interaction with thiophenol and the mercaptoacetate ester[9]; in contrast to the reaction with alcohols, this process takes place only on heating. 2-Mercaptoethyl alcohol adds to perfluoromethacryloyl fluoride, forming 1 : 1 and 1 : 2 adducts[9]:



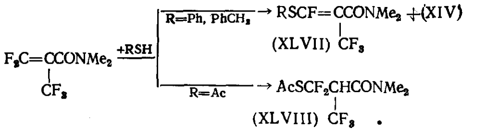
$$\underset{(I)}{F_2C{=}\underset{CF_3}{\underset{|}{C}}{-}COF} + RSH \xrightarrow{100^\circ} RSCF_2\underset{CF_3}{\underset{|}{C}}HCOF;$$

$R{=}Ph,\ MeOCOCH_2;$

$$(I) + HSCH_2CH_2OH \rightarrow HSCH_2CH_2OCF_2\underset{CF_3}{\underset{|}{C}}HCOF + \begin{array}{l} CH_2SCF_2\overset{CF_3}{\overset{|}{C}}HCOF \\ | \\ CH_2OCF_2\underset{CF_3}{\underset{|}{C}}HCOF \end{array} \qquad (17)$$

The "hard" hydroxy-group is apparently somewhat more reactive with respect to the carbon atom of the $CF_2{=}$ group than the "soft" mercapto-group.

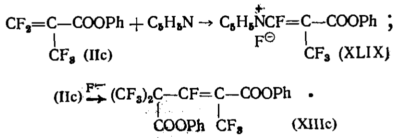
The reaction of **PFMA** dimethylamide with thiophenol or phenylmethanethiol gives the "vinyl" substitution product (**XLVII**) (the *cis*- and *trans*-isomers) together with the HFIBA dimethylamide (**XIV**) (the rate of this reaction is discussed in subsection 2 of this Section). Thioacetic acid reacts readily with **PFMA** dimethylamide, but it gives rise to a mixture of products from which only the thioloacetyl derivative (XLVIII) could be isolated in a low yield[57]:



$$\underset{\displaystyle CF_3}{F_2C{=}CCONMe_2} \xrightarrow{+RSH} \begin{cases} \xrightarrow{R=Ph,\ PhCH_2} \underset{(XLVII)\ CF_3}{RSCF{=}CCONMe_2} + (XIV) \\ \xrightarrow[R=Ac]{} \underset{(XLVIII)\ CF_3}{AcSCF_2CHCONMe_2}\ . \end{cases} \qquad (18)$$

4. Reactions with *N*-Nucleophiles

When PFMA derivatives are acted upon by tertiary amines, they usually dimerise readily (subsection 1 of this Section). For example, phenyl perfluoromethacrylate (IIc) is converted into the dicarboxylate ester (XIIIc) in the presence of a catalytic amount of pyridine at room temperature[10]. Possibly the reaction begins with the substitution of the vinyl fluorine atom by the pyridinium residue and the F^- anion split off then catalyses the dimerisation reaction:

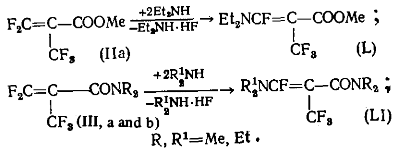


$$\underset{CF_3\ (IIc)}{CF_2{=}C{-}COOPh} + C_5H_5N \rightarrow \underset{F^{\ominus}}{C_5H_5\overset{+}{N}}CF{=}\underset{CF_3\ (XLIX)}{C{-}COOPh}\ ;$$

$$(IIc) \xrightarrow{F^-} (CF_3)_2\underset{COOPh}{C}{-}CF{=}\underset{CF_3}{C}{-}COOPh\ . \quad (XIIIc)$$

However, this mechanism remains purely speculative, since there is no direct evidence for the formation of compounds of type (XLIX). Like tertiary amines, certain carboxylic acid dialkylamides also catalyse the dimerisation of PFMA esters (see subsection 7 of this Section).

The reactions with secondary amines usually lead to the formation of the "vinyl" substitution products (L) and (LI)[59,65]§:

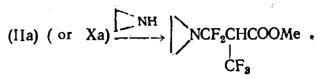


$$\underset{CF_3\ \ (IIa)}{F_2C{=}C{-}COOMe} \xrightarrow[-Et_2NH\cdot HF]{+2Et_2NH} Et_2NCF{=}\underset{CF_3\ \ (L)}{C{-}COOMe}\ ;$$

$$\underset{CF_3\ (III,\ a\ and\ b)}{F_2C{=}C{-}CONR_2} \xrightarrow[-R^1_2NH\cdot HF]{+2R^1_2NH} R^1_2NCF{=}\underset{CF_3\ \ (LI)}{C{-}CONR_2}\ ;$$

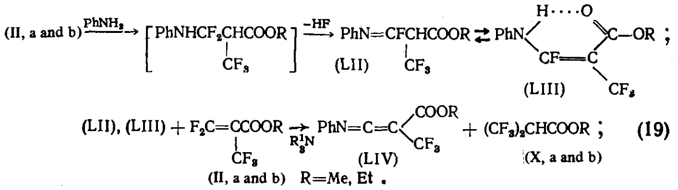
$$R, R^1{=}Me, Et\ .$$

In contrast to dimethyl- and diethyl-amines, aziridine forms an addition product on reaction with the perfluoromethacrylate ester. The same product has been obtained from the HFIBA ester[67]:



Here the PFMA ester behaves like perfluoroisobutene, which reacts with dialkylamines to form substitution products and with aziridine to form addition products[67].

The reaction of perfluoroisobutene with arylamines in the presence of tertiary amines leads to imidoyl fluorides and ketenimines[53]. PFMA esters react with aniline via a similar mechanism, forming imidoyl fluorides (LII) [in the form of tautomeric mixtures with enamines (LIII)] and ketenimines (LIV)[68]:



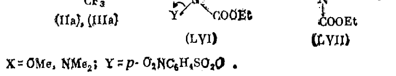
(19)

An excess of the PFMA ester acts in this reaction like a dehydrofluorinating agent. The enamines (LIII) are comparatively stable owing to the hydrogen bond between the NH and COOR groups.

The anion (LV), formed from *p*-nitrobenzenesulphonyloxyurethane on treatment with triethylamine, is an active *N*-nucleophile. Like perfluoroisobutene, methyl perfluoromethacrylate and PFMA dimethylamide readily react with this anion; the resulting carbanions (LVI) are stabilised by cyclisation with elimination of the *p*-nitrobenzenesulphonyloxy-group, readily removed in the form of the anion, and not by the elimination of an F^- anion (as in "vinyl" substitution) or by the capture of a proton (as in an addition reaction). Nucleophilic elimination of PFMA derivatives is thus achieved with formation of substituted aziridines (LVII)[64]:

$$EtOCONHY + R_3N \rightleftarrows EtOCO\overset{-}{N}Y + R_3\overset{+}{N}H\ ;$$

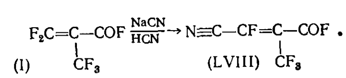
(LV)



The reactions involving the cycloaddition of *N*-nucleophiles such as nitriles and isocyanates to perfluoromethacryloyl fluoride are discussed below in subsection 7.

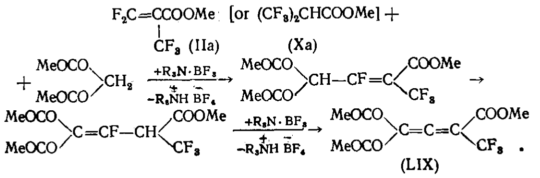
5. Reactions with *C*-Nucleophiles

The "vinyl" substitution product (LVIII) has been obtained in a low yield by the reaction of perfluoromethacryloyl fluoride with the cyanide anion[36]:



$$\underset{(I)\quad CF_3}{F_2C{=}C{-}COF} \xrightarrow[HCN]{NaCN} N{\equiv}C{-}CF{=}\underset{(LVIII)\ CF_3}{C{-}COF}\ .$$

When the malonic ester reacts with the PFMA ester in the presence of the adduct $Et_3N.BF_3$, a "vinyl" substitution product is also formed; isomerisation and subsequent dehydrofluorination lead to 1-trifluoromethyl-1,3,3-tri(methoxycarbonyl)allene (LIX). The same product was obtained also from the HFIBA ester, which is converted into a PFMA ester under the reaction conditions[25]:



As in many other reactions, the PFMA ester behaves here like perfluoroisobutene[69].

Another type of reactions of PFMA derivatives with *C*-nucleophiles involves dimerisation, the vinylfluorine

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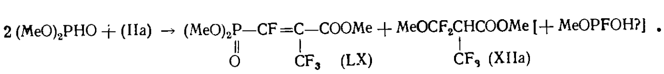
[§] The reaction of perfluoromethacrylonitrile with diethylamine followed by hydrolysis yields the amidonitrile $Et_2NCOCH(CF_3)CN$.[26] On treatment with secondary amines, methyl perfluoroacrylate forms unstable addition products, which undergo further transformations[66].

atom being substituted on treatment with a mesomeric carbanion of type (A), (C), or (D) [Eqns. (2), (4), and (10)].

Certain *C*-nucleophiles are involved in cycloaddition reactions with perfluoromethacryloyl fluoride (see sub-section 7 below).

6. Reactions with *P*-Nucleophiles

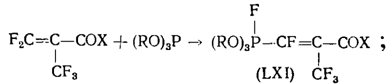
Methyl perfluoromethacrylate reacts with dimethyl phosphite at room temperature, forming the "vinyl" substitution product (LX) together with the methanol addition product (XIIa)[47]:



$$2\,(MeO)_2PHO + (IIa) \rightarrow \underset{\underset{O}{\|}}{(MeO)_2P}-CF=\underset{\underset{CF_3}{|}}{C}-COOMe\ (LX) + MeOCF_2\underset{\underset{CF_3}{|}}{C}HCOOMe\ (XIIa)\ [+ MeOPFOH?]\ .$$

The mechanism of this reaction is obscure.

PFMA esters and dialkylamides react very readily with trialkyl phosphites, forming substituted perfluoroalkenyltrialkoxyfluorophosphoranes (LXI)[47,70]¶:



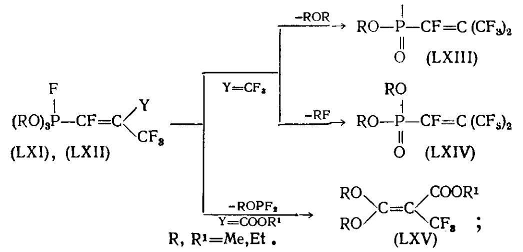
$$F_2C=\underset{\underset{CF_3}{|}}{C}-COX + (RO)_3P \rightarrow (RO)_3\overset{\overset{F}{|}}{P}-CF=\underset{\underset{CF_3}{|}}{C}-COX\ ;\quad (LXI)$$

(II), (III) X=OMe, OEt, NMe$_2$; R=Me, Et .

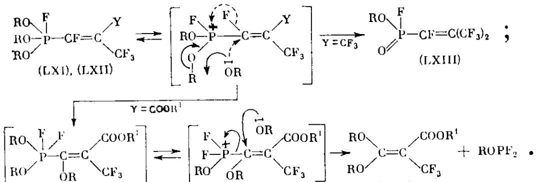
An analogous reaction is known for perfluoroisobutene, which interacts with triethyl phosphite to form a stable intermediate of the Arbuzov rearrangement, namely $(EtO)_3PFCF=C(CF_3)_2$ (LXII).[71] As in the reactions with other nucleophiles, methyl perfluoromethacrylate proved to be more reactive than perfluoroisobutene in the reaction with trimethyl phosphite[46].

The structures of the adducts of trialkyl phosphites with PFMA derivatives [compounds (LXI)] and with perfluoroisobutene [compounds (LXII)] have been confirmed by NMR. The covalent character of the P–F bond leads to spin–spin coupling between the ^{31}P and ^{19}F nuclei (J = 820 Hz).[47,70] The formation of these adducts constitutes a rare instance of the isolation of pentacovalent (and not tetracovalent quasiphosphonium) intermediates of the Arbuzov rearrangement[72].

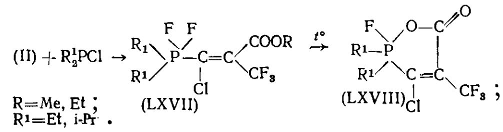
The adducts of perfluoroisobutene with trialkyl phosphite decompose in two ways on heating, forming the products of the Arbuzov rearrangement—the fluoride of the acid ester of perfluoroisobutenylphosphonic acid (LXIII) (as a result of the elimination of an ether)—and the diester (LXIV) (as a result of the elimination of an alkyl fluoride)[47,71]. In contrast to this, the adducts of PFMA esters with trialkyl phosphites are cleaved in an unusual way on heating, forming phosphorus(III) compounds (alkyl phosphorodifluoridites) and acetals of substituted ketens (LXV)[47,70]†:



This sharp difference in behaviour can probably be accounted for by the much more marked electrophilic properties of the carbon atom in the CF= group in the phosphoranes obtained from PFMA esters, compared with the phosphoranes derived from perfluoroisobutene. It is suggested that the first stage in the cleavage of the phosphoranes (LXI) and (LXII) is their reversible dissociation into an anion (RO^- or F^-) and a quasiphosphonium cation. Further reactions depend on which electrophilic centre is attacked by the anion. In the adducts formed from perfluoroisobutene, the carbon atom of the alkyl group R functions as the electrophilic centre, while in adducts obtained from PFMA esters the electrophilic centre is the β-carbon atom of the "acrylic" system. The new phosphorane (LXVI) formed in the latter case dissociates into an anion RO^- and a quasiphosphonium cation; the repeated attack by the alkoxide anion on the β-carbon atom cleaves the molecule into an acetal (LXV) and an alkyl phosphorodifluoridite[46,47]‡:



Thus, owing to the enhanced electrophilic properties of the β-carbon atom, in the decomposition of the adducts of PFMA esters with trialkyl phosphites the substituents at the phosphorus and carbon atoms change places. A similar exchange occurs also in the interaction of PFMA esters with dialkylchlorophosphines, which leads to the phosphoranes (LXVII), containing the PF_2 and CCl= groups [when these phosphoranes are heated, an alkyl fluoride is split off and cyclisation products are obtained—substituted oxaphospholens (LXVIII)][47]:



In contrast to this, the products obtained from chlorodiethylphosphine and perfluoroisobutene retain the CF= group and only bis(dialkylamino)chlorophosphines react with perfluoroisobutene to form compounds $(R_2N)_2PF_2.CCl=C(CF_3)_2$ containing the CCl= group[73].

7. Cycloaddition

The appreciably electrophilic properties of PFMA derivatives are responsible for the ease with which they undergo cycloaddition reactions on treatment with various unsaturated compounds having fairly pronounced nucleophilic properties. PFMA derivatives containing the $>C=\underset{|}{C}-\underset{|}{C}=O$ bond system can be involved in 1,2- or 1,4-cycloaddition reactions, only the C=C bond, and not the

---

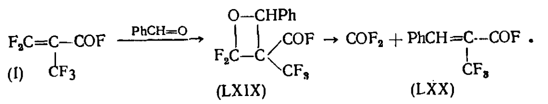
¶The esters of difluoromethylenemalonic acid react similarly[35].

†The adduct of the difluoromethylenemalonic ester with $(MeO)_3P$ is cleaved similarly to $MeOPF_2$ and $(MeO)_2C=C(COOMe)_2$.[35]

‡In the process represented in the above scheme, the nucleophilic participation of the carbonyl group, leading to the intermediate formation of 1,2-oxaphospholen structures, may also play an important role.

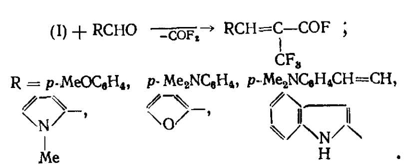
C=O bond, reacting in the former case. Cycloaddition results in the formation of three-, four-, five-, and six-membered rings; it is sometimes possible to isolate only the products of the further reactions of these compounds. The oxygen, nitrogen, and carbon atoms in the reactant can function as the nucleophilic centre.

When perfluoromethacryloyl fluoride reacts with benzaldehyde, a substituted oxetan (LXIX) is formed[9,27,36]. It is relatively unstable, decomposing on heating into carbonyl difluoride and α-trifluoromethylcinnamoyl fluoride (LXX) (a mixture of the *cis*- and *trans*-isomers):



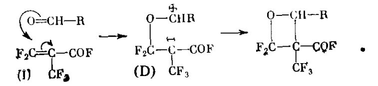
This reaction constitutes a method for the introduction of the substituted methylene group $=C(CF_3)COF$ in place of the oxygen atom of the carbonyl group and, in terms of its final result, it thus resembles the Wittig reaction.

A number of unsaturated acid fluorides have been obtained similarly but without the isolation of the intermediate oxetans[9,74]:



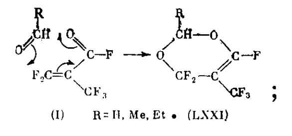
2,6-Dimethyl-γ-pyrone enters into a similar reaction[9].

The mechanism of the 1,2-cycloaddition of carbonyl compounds to perfluoromethacryloyl fluoride probably involves the formation of a dipolar ion (D)[36]:

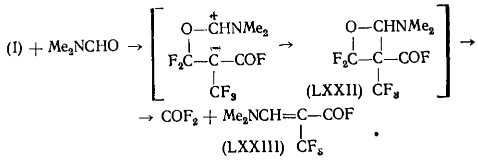


(20)

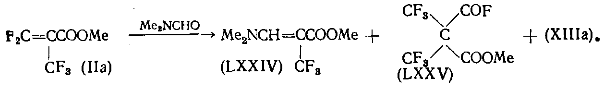
The negative charge in this dipolar ion is stabilised by the electron-withdrawing fluorine-containing groups and the positive charge by the electron-donating mesomeric effect of the group R. On the other hand, if the group R is incapable of stabilising the positive charge on the neighbouring carbon atom, the formation of the dipolar ion becomes unfavourable and synchronous (or almost synchronous) 1,4-cycloaddition takes place instead of the 1,2-cycloaddition. Thus, aliphatic aldehydes add to perfluoromethacryloyl fluoride, giving rise to substituted *m*-dioxins (LXXI)[9,27]:



The presence of the dimethylamino-group, which exhibits a considerable +*M* effect, stabilises the dipolar ion; for this reason, the reaction of perfluoromethacryloyl fluoride with dimethylformamide involves 1,2-cycloaddition with formation of the oxetan (LXXII), which, however, cannot be isolated, since it is immediately cleaved to difluorophosgene and the acid fluoride (LXXIII)[9,74]§:



Methyl perfluoromethacrylate reacts more slowly with dimethylformamide than the acid fluoride. Together with the ester (LXXIV), the reaction also leads to the formation of the acid fluoride (LXXV) and of insignificant amounts of the "dimer" (XIIIa)[46]:

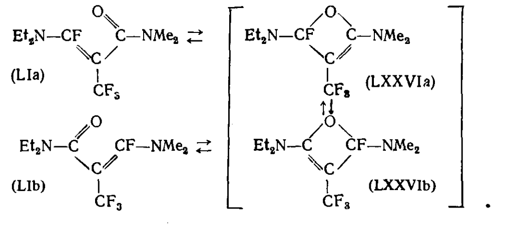


(21)

Evidently the carbonyl difluoride produced adds to the PFMA ester [see Eqn. (11)]. The analogous reaction of dimethylformamide with perfluoroisobutene leads to the enamine $Me_2NCH{=}C(CF_3)_2$ and the acid fluoride $(CF_3)_3COF$.[75] Perfluoroisobutene reacts with dimethylformamide somewhat more slowly than does the PFMA ester[46].

In contrast to dimethylformamide, dimethylacetamide and tetramethylurea do not undergo cycloaddition to methyl perfluoromethacrylate. In the latter case, the initial ester is wholly converted into the "dimer" (XIIIa). PFMA dimethylamide does not react with dimethylformamide[46].

An interesting intramolecular reaction, analogous to the formation of oxetans from PFMA derivatives and dimethylformamide, has been discovered recently. It was found that the dialkylamides of β-dialkylamino-β-fluoro-α-trifluoromethylacrylic acids (LI), containing various alkyl groups at the "amine" and "amide" nitrogen atoms, form on heating to 140°C (or to 100°C in the presence of $Et_3O.BF_3$) an equilibrium mixture containing the isomeric amides (LIa) and (LIb) in proportions of 1 : 1. This evidently involves the intermediate cyclisation of the $\alpha\beta$-unsaturated amides to the substituted oxetens (LXXVI, a and b) (or their adducts with BF_3), the allyl rearrangement with a shift of the F^- ion, and the reverse ring opening reaction[65]:



Methyl β-diethylamino-β-fluoro-α-trifluoromethylacrylate (L) and the dimethylamide of β-fluoro-α-trifluoromethyl-β-phenoxyacrylic acid (XXXVIII) do not undergo this type of isomerisation. Evidently the rearrangement requires both sufficiently pronounced electrophilic properties of the carbonyl oxygen atom attacking the β-carbon atom and sufficient mobility of the fluorine atom, determined by the mesomeric effects of the substituent[65].

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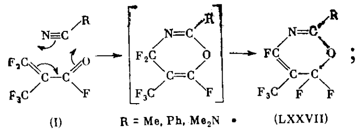
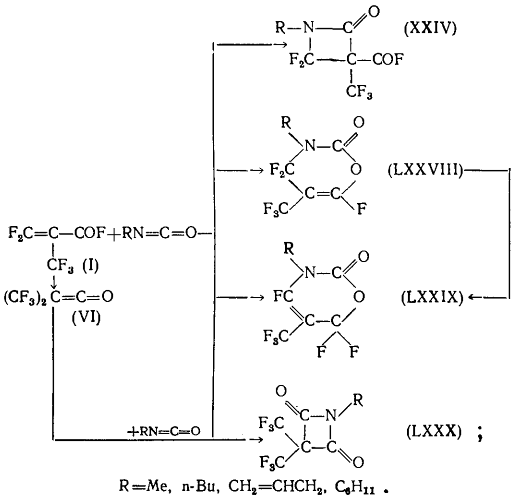
§ A similar reaction of $CF_2{=}CFCOF$ requires somewhat more severe conditions[9].

In contrast to carbonyl compounds, nitriles are involved in 1,4-cycloaddition on interaction with perfluoromethacryloyl fluoride; the subsequent rearrangement leads to substituted 1,3-oxazines (LXXVII)[27,36]:



The reaction with dimethylcyanamide takes place much more readily than those with acetonitrile and benzonitrile.

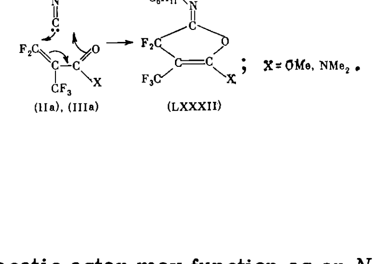
On reaction with perfluoromethacryloyl fluoride, isocyanates form the 1,2-cycloaddition products (XXIV), the 1,4-cycloaddition products (LXXVIII), the allyl rearrangement products (LXXIX), and the products of their cycloaddition to bis(trifluoromethyl)keten (LXXX)[5,27,36]:



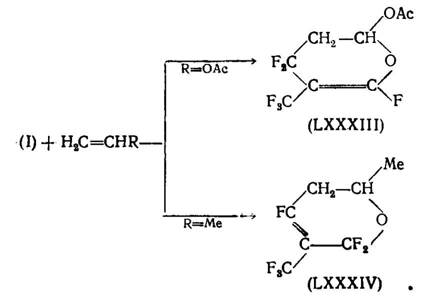
An increase in the polarity of the medium favours 1,2-cycloaddition (via a dipolar ion)[5,27,36].

The diazoacetic ester¶, isonitriles, olefins, phenylacetylene and ketens are *C*-nucleophiles capable of being involved in cycloaddition reactions.

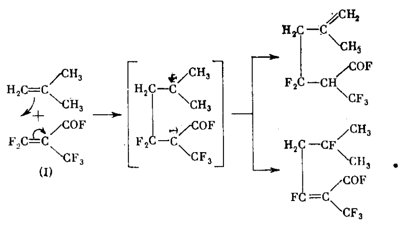
The diazoacetic ester reacts with perfluoromethacryloyl fluoride under mild conditions, giving a substituted cyclopropane (LXXXI) (the *erythro*- and *threo*-isomers)[9]. When cyclohexyl isocyanide reacts with PFMA derivatives, substituted iminodihydrofurans (LXXXII) are formed via 1,4-cycloaddition to the system $\rangle C=\underset{|}{C}-\underset{|}{C}=O$:[77]



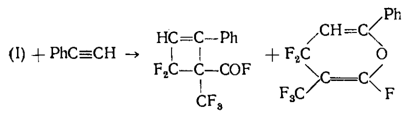
The reaction of perfluoromethacryloyl fluoride with certain olefins leads to six-membered rings via 1,4-cycloaddition; under these conditions, subsequent allyl rearrangement (1,3-migration of the fluorine atom) is frequently observed. The reaction with vinyl acetate leads to the formation of the 1,4-cycloadduct (LXXXIII) and the reaction with propene (and with norbornene) gives the allyl rearrangement product (LXXXIV)[27,36,78]:



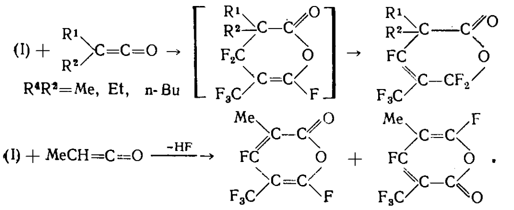
In the reaction with propene, a further two linear products were isolated: $CH_3CHFCH_2CF=C(CF_3)COF$ and $CH_3CH=CHCF=C(CF_3)COF$. Only linear products were obtained after the reaction with isobutene. It may be that, as in the reaction with aromatic aldehydes [Eqn. (20)], a dipolar ion (with the positive charge stabilised by the action of two methyl groups) is formed here as an intermediate, but it does not cyclise to cyclobutane, isomerising with migration of the H⁺ or F⁻ ion[27,36]:



Phenylacetylene adds to perfluoromethacryloyl fluoride, forming 1,2- and 1,4-cycloaddition products[79]:



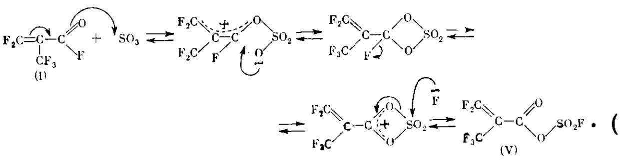
When perfluoromethacryloyl fluoride reacts with dialkylketens, 1,4-cycloaddition to the C=C bond of the keten takes place with subsequent 1,3-migration of the fluorine[27,36]. In the reaction with methylketen, the corresponding dehydrofluorination products were isolated[36]:



¶The diazoacetic ester may function as an *N*-nucleophile (cf. Gambaryan et al.[76]).

8. Other Reactions of PFMA Derivatives

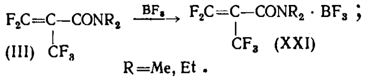
Reactions with electrophilic compounds are completely uncharacteristic of PFMA derivatives. Only sulphur trioxide, a powerful electrophile, is capable of reacting with perfluoromethacryloyl fluoride. In contrast to reactions with nucleophiles, in this case the acyl fluoride group is the most reactive, the product being the mixed anhydride (V). It may be that the reaction begins with attack by the electrophilic SO_3 species on the carbonyl oxygen atom[37]:



(22)

The reaction is reversible—on heating to 125–140° C, the anhydride (V) is cleaved to the initial compounds.

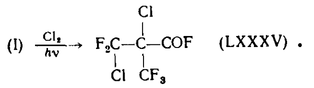
When dialkylamides of PFMA are acted upon by BF_3, the adducts (XXI) are formed [cf. Eqn. (8)][7,33]:



$$\underset{\text{(III)}}{F_2C{=}\underset{\substack{|\\CF_3}}{C}{-}CONR_2} \xrightarrow{BF_3} \underset{\text{(XXI)}}{F_2C{=}\underset{\substack{|\\CF_3}}{C}{-}CONR_2\cdot BF_3}\ ;\quad R{=}Me, Et\,.$$

The attempts to brominate the dialkylamides were unsuccessful—only the HBr addition products were obtained [Eqn. (12)][7].

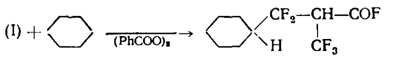
On chlorination, perfluoromethacryloyl fluoride gives rise to $\alpha\beta$-dichloropentafluoroisobutyryl fluoride (LXXXV)[8]:



$$\text{(I)} \xrightarrow[h\nu]{Cl_2} F_2\underset{\substack{|\\Cl}}{C}{-}\overset{\substack{Cl\\|}}{\underset{\substack{|\\CF_3}}{C}}{-}COF \quad \text{(LXXXV)}\,.$$

This reaction is initiated by ultraviolet irradiation and evidently proceeds via a radical mechanism. The use of chlorination for the protection of the reactive $CF_2{=}C{<}$ group is discussed in subsections 1 and 4 of Section II.

In the presence of a radical reaction initiator, cyclohexane readily adds to the C=C bond of perfluoromethacryloyl fluoride[9,37]:



There is little information available about the polymerisation of PFMA derivatives†. Perfluoromethacryloyl fluoride does not apparently polymerise by itself, but it does undergo copolymerisation with other monomers[9,82,83]. The rubber-like copolymer of perfluoromethacryloyl and ethylene, obtained on heating under pressure in the presence of t-butyl peroxide, is soluble in carbon tetrachloride; on treatment with ethylenediamine, a cross-linked polymer, insoluble in carbon tetrachloride, is formed[9,82]. A patent[82] also indicates the possibility of obtaining copolymers from perfluoromethacryloyl fluoride and monomers such as methyl methacrylate, acrylonitrile, tetrafluoroethylene, vinyl fluoride, and vinylidene fluoride. After cross-linking the copolymers can be used for the preparation of films and various coatings, for the impregnation or coating of porous materials, etc. The copolymers of perfluoromethacryloyl fluoride and $CH_2{=}CF_2$, obtained by radiation-induced copolymerisation, are readily cross-linked by bifunctional compounds; they have high thermal stabilities and readily adhere to metals[83].

Ethyl perfluoromethacrylate (IIb) and the diethylamide of PFMA (IIIb) do not polymerise on heating in the presence of benzoyl peroxide, while the dimethylamide (IIIa) forms under these conditions a brittle solid polymer, soluble in acetone and insoluble in carbon tetrachloride. Similar polymers have been obtained from the dimethyl- and diethylamides of PFMA (III, a and b) on γ-irradiation[7].

Examination of the chemical properties of PFMA derivatives reveals distinct electrophilic properties of these compounds. The reactions with very weak nucleophiles, for example with carboxylic acids, which do not require base catalysis, are particularly instructive in this respect. Such reactions are completely uncharacteristic of either perfluoro-olefins or perfluoro-derivatives of $\alpha\beta$-unsaturated carbonyl compounds. Evidently the electrophilic properties of fluoro-olefins and $\alpha\beta$-unsaturated carbonyl compounds are "added together" in the case of PFMA derivatives.

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† For the polymerisation and copolymerisation of perfluoroacrylic acid derivatives, see Refs. 9, 80, and 81.

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The Perfluoro-t-butyl Anion in the Synthesis of Organofluorine Compounds

B.L.Dyatkin (deceased), N.I.Delyagina, and S.R.Sterlin

Methods for the generation and reactions of the perfluoro-t-butyl anion—a convenient model for the investigation of the chemistry of perfluoroalkyl carbanions, are examined. Syntheses based on this anion lead to the formation of a wide variety of compounds containing the $(CF_3)_3C$ group.

The bibliography includes 76 references.

CONTENTS

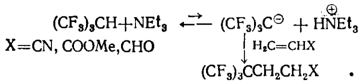
I. INTRODUCTION

Reactions involving perfluoroalkyl carbanions have been acquiring increasing importance in the chemistry of organofluorine compounds, because of the comparatively high thermodynamic stability of such carbanions due to the stabilising effect of the fluorine atoms [1,2]†. The perfluoro-t-butyl anion is particularly stable. Vigorous studies on methods for the preparation of this carbanion and its reactions have led during the last 10 years to the synthesis of a wide variety of compounds containing the $(CF_3)_3C$ group. The two main pathways to the synthesis of the $(CF_3)_3C^-$ anion are heterolysis of the C–H bond in nonafluoroisobutane and the addition of the F^- anion to perfluoroisobutene. Furthermore, it is possible to employ for synthetic purposes di(perfluoro-t-butyl)mercury under the conditions of nucleophilic catalysis.

II. REACTIONS OF NONAFLUOROISOBUTANE IN THE PRESENCE OF TERTIARY AMINES

Nonafluoroisobutane $(CF_3)_3CH$ is a comparatively strong CH acid. (According to various estimates, the pK_a values are approximately 11,[1] approximately 7,[5] or approximately 20.[6]) It is normally unstable when acted upon by bases, readily eliminating fluorine atoms in the form of ions [1]. However, when nonafluoroisobutane is mixed with triethylamine, fluorine atoms are not converted into an inorganic form. It has been observed by ^1H NMR that this entails the formation of a comparatively strong hydrogen bond between the molecules of nonafluoroisobutane and triethylamine with participation of the hydrogen atom of the methine group (the chemical shift due to the hydrogen bond amounts to 1.95 p.p.m.)[7].

Although a signal due to the $(CF_3)_3C^-$ carbanion cannot be detected in the ^1H NMR spectrum, its presence in the mixture can be demonstrated by reactions with various electrophiles [8]. Thus nonafluoroisobutane can be made to take part in the Michael reaction. In the presence of triethylamine, it readily adds to the C=C bonds of acrylic systems—acrylonitrile, methyl acrylate, and acrolein[9,10]:



$$\begin{tikzcd}(CF_3)_3CH + NEt_3 \arrow[r, shift left] & (CF_3)_3C^{\ominus} + H\overset{\oplus}{N}Et_3 \arrow[l, shift left] \arrow[d, "H_2C=CHX"] \\ X=CN, COOMe, CHO & (CF_3)_3CCH_2CH_2X \end{tikzcd}$$

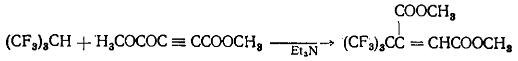
(I)

Further reactions of products (I) led to the formation of various compounds containing the $(CF_3)_3C$ group, such as

$(CF_3)_3CCH_2CH_2COOH$, $(CF_3)_3CCH_2CH_2CH_2OH$, $(CF_3)_3CCH_2CH_2CH_2SH$, $(CF_3)_3CCH_2CH_2CH_2NH_2$ etc. (Ref.10).

The addition to the activated triple bond C≡C of benzoylaetylene or the acetylenedicarboxylate ester takes place just as readily [11]:

$$(CF_3)_3CH + HC\equiv CCOPh \xrightarrow[Et_3N]{} (CF_3)_3CCH=CHCOPh\ ;$$

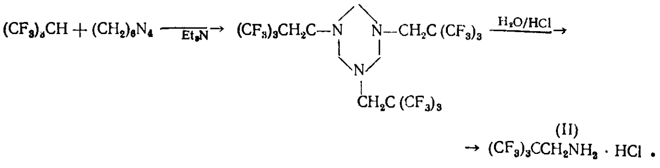


$$(CF_3)_3CH + H_3COCOC\equiv CCOOCH_3 \xrightarrow[Et_3N]{} (CF_3)_3C\overset{\displaystyle COOCH_3}{\overset{|}{C}}=CHCOOCH_3\ .$$

Nonafluoroisobutane is involved in hydroxymethylation and aminomethylation reactions [8,12]. When it was heated with paraformaldehyde in the presence of triethylamine, a low yield of perfluoro-t-butylmethanol was obtained:

$$(CF_3)_3CH + (CH_2O)_n \xrightarrow[Et_3N]{} (CF_3)_3CCH_2OH\ .$$

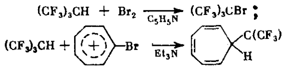
Its reaction with urotropine gave a substituted triazine (II) whose hydrolysis led to the hydrochloride of perfluoro-t-butylmethylamine:



(II)

Ionic halogenation [13] and tropylation [14] of nonafluoroisobutane have also been achieved:

$$(CF_3)_3CH + Br_2 \xrightarrow[C_5H_5N]{} (CF_3)_3CBr\ ;$$



The attempt to alkylate nonafluoroisobutane by ethyl iodide in the presence of triethylamine was unsuccessful, probably because of the formation of tetraethylammonium iodide, which is incapable of alkylating monohydroperfluoroalkanes under the reaction conditions [8].

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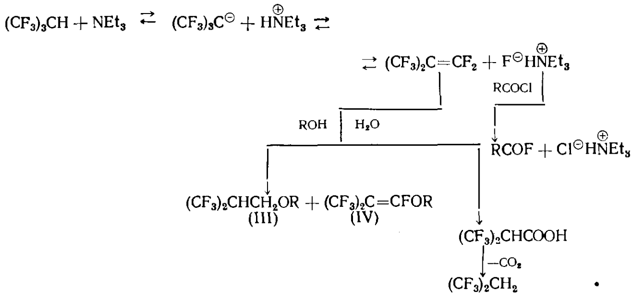
†For a discussion of the possible role of the "negative hyperconjugation" in the stabilisation of fluoro-carbanions, see Refs. 1, 3, and 4.

The benzoylation of nonafluoroisobutane could not be achieved either. On treatment with benzoyl chloride in the presence of triethylamine, it is dehydrofluorinated, yielding perfluoroisobutane[15]:

$$(CF_3)_3CH + PhCOCl + Et_3N \rightarrow (CF_3)_2C{=}CF_2 + PhCOF + Et_3\overset{\oplus}{N}HCl^{\ominus} .$$

Evidently, when nonafluoroisobutane is mixed with triethylamine, it is dehydrofluorinated, but the reaction is reversible, the equilibrium being almost completely displaced towards the starting materials (see above). Benzoyl chloride can participate in a reversible exchange reaction with triethylamine hydrofluoride, which shifts the equilibrium towards the formation of perfluoroisobutene[8,15]. A similar shift of the equilibrium can be achieved by removing perfluoroisobutene from the reaction instead of triethylamine hydrofluoride. Thus when nonafluoroisobutane reacts with methanol in the presence of triethylamine, the products are the stable ethers (III) and (IV).[15] If water is used instead of methanol, one obtains 1,1,1,3,3,3-hexafluoropropane as a result of the decarboxylation of 2,2,2-trifluoro-2-trifluoromethylpropionic acid (α-hydrohexafluoroisobutyric acid)[16]:

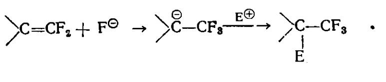


All these reactions take place with the intermediate formation of the perfluoro-t-butyl anion.

Thus the use of the carbanion $(CF_3)_3C^-$ generated from nonafluoroisobutane gives rise to fairly considerable synthetic possibilities. However, another method for the preparation of this carbanion—by the addition of the fluoride anion to perfluoroisobutene—is much more important for the synthesis of organofluorine compounds.

III. REACTIONS OF PERFLUOROISOBUTENE IN THE PRESENCE OF ALKALI METAL FLUORIDES

Perfluoro-olefins occupy an especially important place in the chemistry of organofluorine compounds. Owing to the electron-accepting effect of the fluorine atoms, they exhibit very marked electrophilic properties[17]. One of the most interesting reactions of perfluoro-olefins, which is being very vigorously investigated at the present time, is that with various electrophiles in the presence of fluoride ions in aprotic polar solvents. According to current ideas, the first step in this process is nucleophilic addition of the fluoride ion to the double bonds of the perfluoro-olefin with formation of a perfluoroalkyl carbanion, which then reacts with the electrophile[18]:

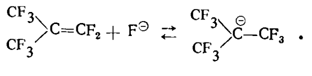


$$>C{=}CF_2 + F^{\ominus} \rightarrow >\overset{\ominus}{C}{-}CF_3 \xrightarrow{E^{\oplus}} >\underset{\displaystyle E}{\underset{|}{C}}{-}CF_3 .$$

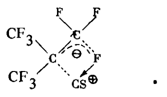
The perfluoro-olefin–alkali metal fluoride system can be regarded as a perfluoroalkyl derivative of the alkali metal. Such systems are involved in a wide range of reactions, the synthetic value of which not only largely compensates the limited applicability of perfluoroalkyl Grignard reagents, but also gives rise to additional possibilities, associated, in particular, with the use of processes such as the Wurtz reaction.

Reactions of this kind were investigated previously mainly in relation to fluorine-containing ethylenes and perfluoropropene. However, the perfluoro-t-butyl anion, obtained from perfluoroisobutene, is a more convenient model for the investigation of the reactions of perfluoroalkyl carbanions. Its advantages are due to a series of factors, including the low tendency of perfluoroisobutene towards dimerisation and oligomerisation‡ and its pronounced electrophilic properties, which ensure the ease of addition of the fluoride ion. In contrast to other perfluoroalkyl carbanions, the generation of the perfluoro-t-butyl anions can be observed directly with the aid of ^{19}F NMR spectra[22].

Two characteristic multiplets, corresponding to the CF_3 and CF_2 groups (−18 and 20 p.p.m. relative to CF_3COOH), in the perfluoroisobutene spectrum are converted after the addition of caesium fluoride into a broadened singlet displaced downfield (−27 p.p.m.) relative to the CF_3COOH signal. This reaction constitutes a rapid exchange, since the above spectral change is caused by much less than the equivalent amount of caesium fluoride:



The downfield signal shift can be accounted for by a reverse redistribution of electron density via fluorine atoms to the vacant inner orbitals of the metal atom:



The perfluoro-t-butyl anion generated from perfluoroisobutene readily combines with a proton. Thus the reaction of perfluoroisobutene with hydrogen fluoride in the presence of catalytic amounts of ammonium fluoride[23] or triethylamine[15] leads to the formation of nonafluoroisobutene:

$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-F^{\ominus}]{+HF} (CF_3)_3CH .$$

This reaction makes it possible to use perfluoroisobutene as a dehydrofluorinating agent[24,25].

The nucleophilic fluoroiodination of perfluoroisobutene leads to iodoperfluoroisobutane[26]:

$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-I^{\ominus}]{+I_2} (CF_3)_3CI .$$

The same compound has been obtained by the reaction of perfluoroisobutene with iodine monofluoride[27].

The alkylation of the perfluoro-t-butyl anion by various alkyl halides gives rise to considerable possibilities for the synthesis of various organic compounds containing the perfluoro-t-butyl group[22,28]:

$$(CF_3)_2C{=}CF_2 + RX \xrightarrow{CsF} (CF_3)_3C{-}R ;$$

$$R{=}CH_3,\ C_4H_9,\ CH_2{=}CHCH_2;$$

$$C_6H_5CH_2,\ n\text{-}FC_6H_4CH_2,\ (C_6H_5)_2CH;$$

$$X{=}Cl,\ Br,\ I .$$

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‡It is claimed, incidentally, that perfluoroisobutene is dimerised on treatment with CsF in ether or diglyme.[19-21]

3-Bromocyclohexene reacts similarly[22].

It is readily seen that the results of these reactions are similar to those of the Wurtz reaction; at the same time the lower reactivity of the anion $(CF_3)_3C^-$ compared with hydrocarbon carbanions makes it possible to substitute the halogen in compounds containing other reaction centres, for example in β-bromopropionitrile[28], ethylbromoacetate[29], and β-bromoethyl acetate[30]. The reaction with 1,2-dibromoethane under mild conditions leads to the formation of the product resulting from the substitution of one bromine atom by the $(CF_3)_3C$ group[30]:

$$(CF_3)_3C^{\ominus} + BrCH_2X \xrightarrow[-Br^{\ominus}]{} (CF_3)_3CCH_2X\ ;$$

$$X{=}CH_2CN,\ CH_2COOEt,\ CH_2OAc,\ CH_2Br\ .$$

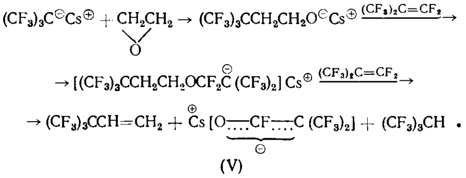
Perfluoro-t-butylacetic acid $(CF_3)_3CCH_2COOH$ was obtained by the hydrolysis of the corresponding ester. The dissociation constant of the acid has been determined and the Taft constant σ* for the $(CF_3)_3C$ group (1.48) has been calculated[31]. This value proved to be much smaller than the additive constant ($\sigma^*_{(CF_3)_3C} = 3\sigma^*_{CF_3} \times 0.357 = 2.79$).

Perfluoro-t-butylethylene has been obtained by the dehydrobromination of 2-(perfluoro-t-butyl)ethyl bromide with solid alkali or by the pyrolysis of 2-(perfluoro-t-butyl)ethyl acetate[30]:

$$(CF_3)_3CCH_2CH_2Y \xrightarrow[-HY]{} (CF_3)_3CCH{=}CH_2\ ;$$

$$Y{=}Br,\ OAc\ .$$

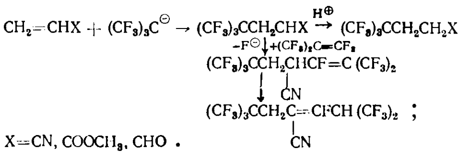
The same olefin is formed together with nonafluoroisobutane and the salt (V), containing a mesomeric anion, is formed when perfluoroisobutene reacts with oxiran in the presence of caesium fluoride[32]:



(V)

Here perfluoroisobutene behaves not only as a dehydrofluorinating agent but also as a kind of dehydrating agent. Under other conditions, perfluoro-t-butylethanol $(CF_3)_3CCH_2CH_2OH$ was isolated from the reaction mixture (after acidification).

Derivatives of perfluoro-t-butylpropionic acid have been obtained by the reaction of the perfluoro-t-butyl anion with derivatives of acrylic acid; in the case of acrylonitrile, the product of further interaction of the intermediate carbanion with a molecule of perfluoroisobutene is also formed[28]:



$$CH_2{=}CHX + (CF_3)_3C^{\ominus} \rightarrow (CF_3)_3CCH_2\overset{\ominus}{C}HX \xrightarrow{H^{\oplus}} (CF_3)_3CCH_2CH_2X$$

$$(CF_3)_3CCH_2\overset{\ominus}{C}HX \xrightarrow[-F^{\ominus}]{+(CF_3)_2C=CF_2} (CF_3)_3CCH_2\underset{\substack{|\\CN}}{C}HCF{=}C(CF_3)_2 \rightarrow (CF_3)_3CCH_2\underset{\substack{|\\CN}}{C}{=}CFCH(CF_3)_2\ ;$$

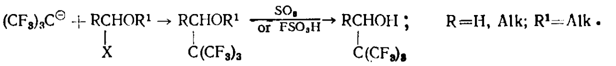
$$X{=}CN,\ COOCH_3,\ CHO\ .$$

Perfluoropropene and tetrafluoroethylene react with carbon dioxide in the presence of caesium fluoride to form perfluoroisobutyric and perfluoropropionic acids respectively. The attempt to synthesise perfluoropivalic acid by carboxylating the perfluoro-t-butyl anion was unsuccessful[19]. Perfluoropivaloyl fluoride $(CF_3)_3CCOF$ is formed together with the enamine (VI) when perfluoroisobutene reacts with dimethylformamide, evidently as a result of the addition of carbonyl difluoride to perfluoroisobutene[33]:

$$(CF_3)_2C{=}CF_2 + OCHN(CH_3)_2 \rightarrow \underset{(VI)}{(CF_3)_2C{=}CHN(CH_3)_2} + (CF_3)_3CCOF\ ;$$

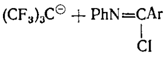
$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-F^{\ominus}]{+COF_2} (CF_3)_3COF\ .$$

Carbonyl difluoride adds to perfluoro-olefins in the presence of CsF or KF.[34-36] The perfluoroethyl and perfluoroisopropyl anions interact with carbonyl compounds, forming fluorinated alcohols[37-39]. The corresponding alcohols containing the $(CF_3)_3C$ group have been obtained by an indirect procedure—via α-halogenoethers[40]:



$$(CF_3)_3C^{\ominus} + \underset{\substack{|\\X}}{RCHOR^1} \rightarrow \underset{\substack{|\\C(CF_3)_3}}{RCHOR^1} \xrightarrow[\text{or } FSO_3H]{SO_3} \underset{\substack{|\\C(CF_3)_3}}{RCHOH}\ ; \quad R{=}H,\ Alk;\ R^1{=}Alk\ .$$

The acylation of the perfluoro-t-butyl anion has not been described (if one disregards the synthesis of perfluoropivaloyl fluoride from perfluoroisobutene and dimethylformamide; see above). However, the anion $(CF_3)_3C^-$ reacts readily with aromatic imidoyl halides:



$$(CF_3)_3C^{\ominus} + PhN{=}\underset{\substack{|\\Cl}}{C}Ar \rightarrow PhN{=}\underset{\substack{|\\C(CF_3)_3}}{C}Ar\ .$$

The attempts to obtain ketones by the hydrolysis of the products of this reaction proved unsuccessful[40].

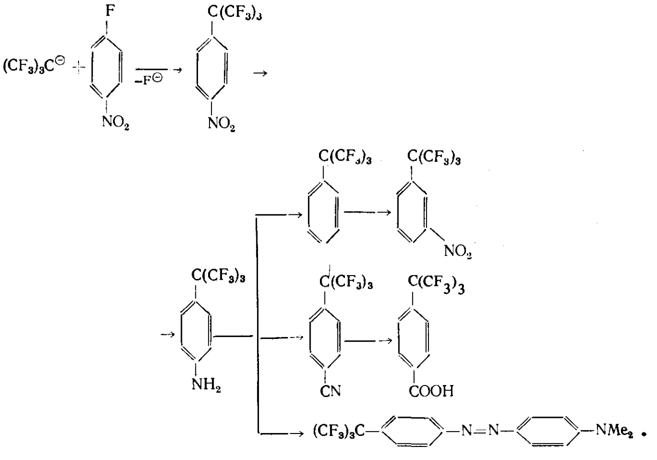
The perfluoro-t-butyl anion can substitute the chlorine atom in 1-chloroacetylenes containing a fairly electronegative substituent in the 2-position[41]. Thus 1-chloro-3,3,3-trifluoropropyne reacts with the ion $(CF_3)_3C^-$ in diglyme at room temperature and chloro(phenyl)acetylene reacts at 120°C:

$$(CF_3)_3C^{\ominus} + ClC{\equiv}CR \rightarrow (CF_3)_3CC{\equiv}CR\ ;$$

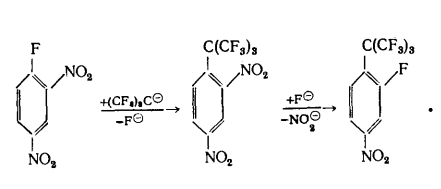
$$R{=}CF_3,\ Ph\ .$$

On the other hand 1-chlorohex-1-yne and 1-chloro-2-methoxyethyne do not react with perfluoroisobutene and caesium fluoride even under severe conditions. The perfluoroisopropyl anion does not react with either 1-chloro-3,3,3-trifluoropropyne or 1-chloro-2-phenylethyne.

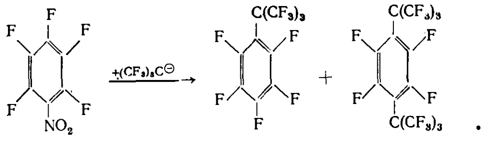
The introduction of the perfluoro-t-butyl group into an aromatic or heterocyclic ring is of definite theoretical interest in connection with the electronic and steric features of the structure of this group. The interaction of the anion $(CF_3)_3C^-$ with various aromatic and heterocyclic compounds containing a mobile halogen atom leads to the corresponding perfluoro-t-butyl substituted derivatives[42]. Thus *p*-nitro(perfluoro-t-butyl)benzene has been obtained from *p*-fluoronitrobenzene and has been used to synthesise various substituted benzenes containing the $(CF_3)_3C$ group[31]:



When the 1-fluoro-2,4-dinitrobenzene is acted upon by the perfluoro-t-butyl anion, the fluorine atom is initially substituted by the $(CF_3)_3C$ group and then the *ortho*-nitro-group, displaced from coplanarity with the benzene ring, is substituted by fluorine on being acted upon by the fluoride ion:

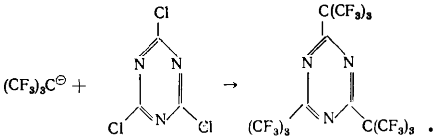


The substitution products (VII) and (VIII) have been isolated in the reaction with pentafluoronitrobenzene:

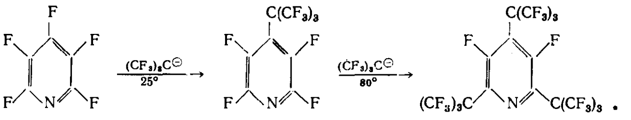


(VII) (VIII)

All three chlorine atoms are substituted in cyanuric acid chloride:



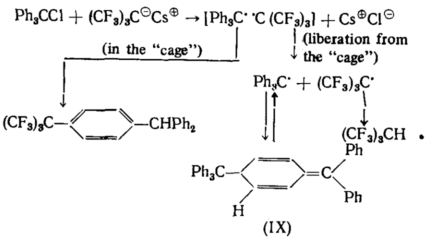
Depending on the conditions, the reaction with perfluoropyridine yields products obtained by the substitution of one or three fluorine atoms:



The interaction of the perfluoro-t-butyl anion with triarylmethyl halides constitutes a special case[42,43]. The reaction with chlorotriphenylmethane proceeds very readily, the chlorine atom being substituted by the perfluoro-t-butyl group. However, this is not direct substitution: the perfluoroalkyl group enters the *para*-position of one of the benzene rings:

An ESR study of this reaction (in diglyme) showed that free triphenylmethyl radicals are formed. In the presence of triphenylmethyl chloride, the concentration of the free radicals passes through a maximum and then approaches the value determined by the constant for the equilibrium between the radical and its diamagnetic dimer [Gomberg's "hexaphenylethane" (IX)].

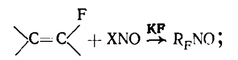
The one-electron transfer stage constitutes a general problem for nucleophilic substitution reactions[44]. The reaction of triphenylmethyl chloride with the perfluoro-t-butyl anion is the first example of proven electron transfer from a perfluoroalkyl anion. The main reaction product is formed within the cage; the triphenylmethyl radicals emerging from the cage are detected by ESR. The perfluoro-t-butyl radicals leaving the cage abstract hydrogen atoms from the solvent and form nonafluoroisobutane. The overall reaction mechanism can be represented as follows:



(IX)

Electron transfer is also observed in the interaction with tri-(p-nitrophenyl)methyl bromide, which results in the formation of the radicals $(p\text{-}O_2NC_6H_4)_3\dot{C}$ and $(CF_3)_3\dot{C}$. Since the tri-(p-nitrophenyl)methyl radical is incapable of dimerisation or recombination, both radicals emerge from the cage. The only organofluorine reaction product is nonafluoroisobutane; the substituted triphenylmethyl radical is stable in the absence of air[43].

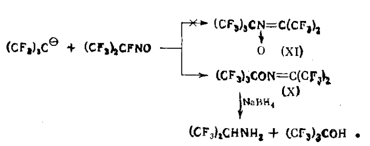
There are many other reactions for which one-electron transfer has not so far been demonstrated but is extremely probable§. Evidently the mechanism of the reaction of the perfluoro-t-butyl anion with nitrosoperfluoroalkanes can be treated from the same standpoint. It appeared strange that, in the reaction of perfluoroalkyl carbanions with nitrosyl fluoride[45,46] or nitrosyl chloride[47], further interaction of the perfluoroalkyl carbanions with the nitrosoperfluoro-compounds formed is not observed:



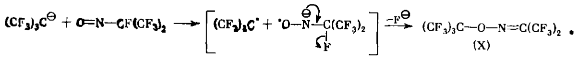
$$>C=CF< + XNO \xrightarrow{KF} R_FNO;$$

$R_F=C(CF_3)_3$, $CF(CF_3)_2$, cyclo-C_4F_7.

Subsequent studies showed that only the perfluoro-t-butyl anion is capable of involvement in the reaction with nitrosoperfluoroalkanes and only when the nitroso-group in the nitrosoperfluoro-compound is attached to a primary or secondary carbon atom[48,49]. The study of the chemical properties of the product of the reaction of the perfluoro-t-butyl anion with 2-nitrosoperfluoropropane, in particular its reduction with sodium tetrahydroborate, established that it has the structure of the N-perfluoro-t-butyl derivative of hexafluoroacetone oxime (X)[48] and not the perfluoronitrone (XI), as suggested previously[49]:



This unusual course of the reaction (attack by the carbanion directed to the negatively charged oxygen atom and not to the positively charged nitrogen atom, as might have been expected) can be explained if it is assumed that the first stage in this reaction is one-electron transfer from the perfluoroalkyl carbanion to the nitroso-group; the final product is then formed as a result of the elimination of the fluoride ion from the α-position relative to the nitrogen atom:



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§For a discussion of the reactions of perfluoroisobutene with haloforms in the presence of the F^- ion, see the review by I. L. Knunyants and V. R. Polishchuk in this issue.

Nitrosoperfluoroisobutane without a fluorine atom in the α-position does not react with a perfluoroalkyl carbanion under comparable conditions. In the synthesis of 2-nitrosoperfluoropropane from perfluoropropene and a nitrosyl halide, the subsequent reaction of the anion $(CF_3)_2CF^-$ with nitroso-compounds is apparently unable to compete with the dimerisation and oligomerisation reactions of perfluoropropene.

The formation of difluoro(perfluoro-t-butyl)amine in the reaction of perfluoroisobutene with tetrafluorohydrazine in the presence of potassium fluoride can also be treated as a one-electron transfer[50]:

$$(CF_3)_2C{=}CF_2 + N_2F_4 \xrightarrow[150^\circ]{KF} (CF_3)_3C{-}NF_2 + N_2 + NF_3\,.$$

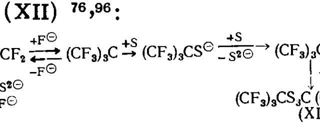
In this case, the perfluoro-t-butyl anion is oxidised by the difluoroamino-radical:

$$(CF_3)_3C^{\ominus} \xrightarrow[\overset{\ominus}{-NF_2}]{+\dot{N}F_2} (CF_3)_3C^{\cdot} \xrightarrow{+\dot{N}F_2} (CF_3)_3C{-}NF_2\,.$$

The range of reactions for which a one electron transfer mechanism is extremely probable¶ can be supplemented by the interaction of perfluoroalkyl carbanions with diazonium salts leading to arylazoperfluoroalkanes[52,53]:

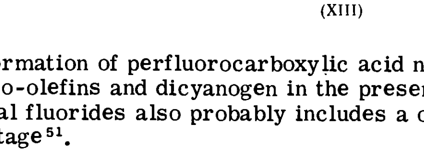
$$R_F^{\ominus} + N{\equiv}\overset{\oplus}{N}{-}C_6H_5 \rightarrow R_F{-}N{=}N{-}C_6H_5 + Cl^{\ominus}\,;$$
$$Cl^{\ominus}$$
$$R_F{=}(CF_3)_3C,\ (CF_3)_2CF,\ \text{cyclo-}C_4H_7\,.$$

Like other perfluoroalkyl anions, the perfluoro-t-butyl anion reacts with elemental sulphur under relatively mild conditions. Generally speaking, the reactions of perfluoroalkyl carbanions with sulphur proceed in different ways, leading to a wide variety of sulphur derivatives, the formation of which may be accounted for by the reactions of the perfluoroalkylmercaptide anions formed initially[54-57,76]. Depending on the structure of the initial olefin and the reaction conditions, these species can undergo the following transformations: (a) they can eliminate a fluoride anion from the α-position relative to the sulphur atom, forming a perfluorothiocarbonyl compound; (b) they can be oxidised by sulphur to a perfluoroalkanethiyl radical and can give rise to di(perfluoroalkyl) di- and poly-sulphides; (c) they can react with the fluoro-olefin via the vinyl substitution mechanism, forming an alkenyl perfluoroalkyl sulphide:



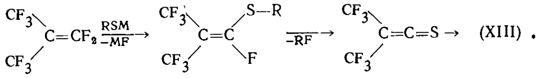
$$R_F^{\ominus} + S \rightarrow R_FS^{\ominus}\,;$$
$$\text{(a)}\ {-}\underset{F}{\overset{|}{\underset{|}{C}}}{-}S^{\ominus} \xrightarrow[-F^{\ominus}]{} {>}C{=}S\,;$$
$$\text{(b)}\ R_FS^{\ominus} \xrightarrow[-S^{2\ominus}]{+S} R_FS^{\cdot} \rightarrow R_FS_nR_F\,;$$
$$\text{(c)}\ R_FS^{\ominus} + CF_2{=}C{<} \xrightarrow[-F^{\ominus}]{} R_FSCF{=}C{<}\,.$$

In the case of perfluoroisobutene, the possibility of the elimination of a fluoride ion from the α-position is ruled out. The perfluoro-t-butylmercaptide anion is oxidised to the corresponding radical, which is converted into the trisulphide (XII); the sulphide ion formed interacts with perfluoroisobutene, forming the dimer of bis(trifluoromethyl)thioketen (XII)[76,96]:

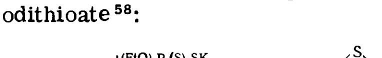


(XIII)

The reaction of perfluoroisobutene with potassium sulphide[57] or with salts of thiolic acids constitutes a preparative method for the synthesis of the thioketen dimer (XIII)[58,59]:

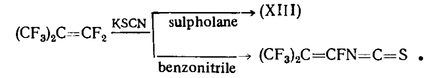


The best result was obtained with potassium diethyl phosphorodithioate[58]:

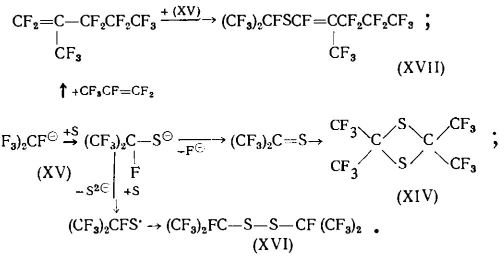


(XIII)

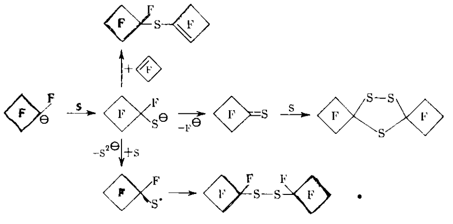
It is interesting to note, that, when this reaction is carried out with potassium thiocyanate, the thiocyanate ion exhibits the properties of an ambident nucleophile[60]:



In the presence of catalytic amounts of potassium fluoride, perfluoropropene gives a satisfactory yield of virtually only one sulphur-containing product—the dimer of perfluorothioacetone (XIV), which is formed as a result of the elimination of the F^- ion from the perfluoroisopropylmercaptide ion (XV); in the presence of large amounts of potassium fluoride, there is a significant increase of the yield of the disulphide (XVI) and of the unsaturated sulphide (XVII)[76]:



The reaction of perfluorocyclobutene with sulphur and KF leads to a similar result, but in this instance the elimination of the fluoride ion from the perfluorocyclobutylmercaptide anion is somewhat difficult, because the formation of perfluorothiocyclobutanone (XVIII)—a compound with a semicyclic double bond—is energetically less favourable; accordingly there is an increase in the yield of compounds containing the perfluorocyclobutylthio-group, i.e. the unsaturated sulphide (XIX) and the disulphide (XX)[56,76]:



(XIX)

(XX)

The reactions of perfluoroalkyl carbanions give rise to considerable possibilities for the preparation of fluorine-containing organomercury compounds[61-63]. In contrast to the electrophilic mercuration reaction known previously[54,64-66], such reactions may be called "nucleophilic mercuration of fluoro-olefins". Depending on the nature of the reagent and the reactions conditions, they make it possible to obtain fully substituted or mixed

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¶The formation of perfluorocarboxylic acid nitriles from fluoro-olefins and dicyanogen in the presence of alkali metal fluorides also probably includes a one-electron transfer stage[51].

perfluoroalkyl derivatives of mercury. Thus perfluoroisobutene reacts with mercury trifluoroacetate in the presence of KF, giving a high yield of di(perfluoro-t-butyl)-mercury and the reaction with trifluoromethylmercury trifluoroacetate leads to trifluoromethyl(perfluoro-t-butyl)mercury [63]:

$$(CF_3)_2C{=}CF_2 + KF \longrightarrow \left| \begin{array}{l} \xrightarrow{Hg(OCOCF_3)_2} [(CF_3)_3C]_2Hg \\ \xrightarrow{CF_3HgOCOCF_3} (CF_3)_3C{-}Hg{-}CF_3\,. \end{array} \right.$$

It is noteworthy that fluorides—HgF_2 and phenylmercury fluoride—add to perfluoroisobutene in the absence of a catalyst [62], behaving themselves as sources of the fluoride ion; one cannot, however, rule cut the possibility that the addition can proceed in this case also via a cyclic four-centre mechanism.

The reaction of perfluoroisobutene with mercury(II) chloride in the presence of KF proceeds less vigorously and stops at the stage involving the formation of perfluoro-t-butylmercury chloride [62]:

$$(CF_3)_2C{=}CF_2 + HgCl + KF \xrightarrow[DMF]{} (CF_3)_3CHgCl \not\longrightarrow \left[(CF_3)_3C\right]_2Hg\,.$$

Evidently the more covalent character of the Hg–Cl bond compared with the Hg–F and Hg–$OCOCF_3$ bonds is manifested here.

In contrast to perfluoroisobutene, perfluoropropene acted upon by potassium fluoride and mercury(II) chloride can form, depending on the reaction conditions, both fully substituted and mixed derivatives of mercury: the reaction in dimethylformamide leads to di(perfluoroisopropyl)-mercury and that in the less polar dimethoxyethane yields perfluoroisopropylmercury chloride [62]:

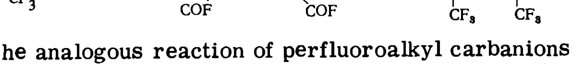
$$CF_3CF{=}CF_2 + HgCl_2 + KF \longrightarrow \left| \begin{array}{l} \xrightarrow{DMF} [(CF_3)_2CF]_2Hg \\ \xrightarrow{DME} (CF_3)_2CFHgCl\,. \end{array} \right.$$

The formation of the symmetrical compound indicates a higher reactivity of the perfluoroisopropyl anion compared with the perfluoro-t-butyl anion. This is confirmed directly by the displacement of perfluoroisobutene from perfluoro-t-butylmercury chloride on treatment with perfluoropropene in the presence of KF [62]:

$$\begin{array}{l} CF_3CF{=}CF_2 + (CF_3)_3CHgCl \xrightarrow{F^{\ominus}} [(CF_3)_2CF]_2Hg + Cl^{\ominus} + (CF_3)_3C^{\ominus} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (CF_3)_2C{=}CF_2 + F^{\ominus}\,. \end{array}$$

Fluoro-olefins containing not only a terminal double bond but also an inner double bond can be involved in the nucleophilic mercuration reaction. Thus perfluorocyclobutene, the mercuration of which could not be achieved under the conditions of the electrophilic reaction [65], in the presence of KF interacts with mercury(II) fluoride and chloride, forming respectively di(perfluorocyclobutyl)-mercury and perfluorocyclobutyl mercury chloride [62]:

Bis(trifluoromethyl)keten, a powerful electrophile, combines with mercury(II) fluoride in the absence of a catalyst [67]. Treatment of the adduct with potassium carbonate leads to the formation of di(perfluoroprop-2-enyl) mercury:



$$(CF_3)_2C{=}C{=}O \xrightarrow{HgF_2} (CF_3)_2(COF)C{-}Hg{-}C(CF_3)_2(COF) \xrightarrow[-COF_2]{K_2CO_3} CF_2{=}C(CF_3){-}Hg{-}C(CF_3){=}CF_2\,.$$

The analogous reaction of perfluoroalkyl carbanions with silver salts can be used to synthesise various perfluoroalkyl derivatives of silver. These compounds were obtained for the first time by the addition of silver fluoride to fluoro-olefins [68-71]; the fluoro-olefin–fluoride ion–$AgOCOCF_3$ system is, however, much more effective. Together with perfluoroisobutene, perfluoropropene, and perfluorocyclobutene, it proved possible to introduce into this reaction chlorotrifluoroethylene [72],[73]:

$$\left.\begin{array}{r} (CF_3)_2C{=}CF_2 \\ CF_3CF{=}CF_2 \\ cyclo\text{-}C_4F_6 \\ CF_2{=}CFCl \end{array}\right\} + MF + AgOCOCF_3 \rightarrow \left\{\begin{array}{l} (CF_3)_3CAg \\ (CF_3)_2CFAg \\ cyclo\text{-}C_4H_7Ag \\ CF_3CFClAg \end{array}\right. ;$$

$$M{=}K,\, Cs\,.$$

On the other hand, the attempt to add silver fluoride as such to chlorotrifluoroethylene was unsuccessful [68], Evidently, silver fluoride, which is a fairly covalent compound, adds via a four-centre mechanism, while in the case of a perfluoroalkyl carbanion only an ionic reaction takes place.

A ^{19}F NMR study of compounds R_FAg showed that exchange reactions involving perfluoroisopropylsilver are much slower than those involving perfluoro-t-butylsilver [73]. This difference can be explained by the coordination of the lone electron pairs of the fluorine atoms in the α-position of perfluoroisopropylsilver to the vacant electronic orbitals of the silver atoms.

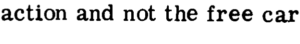
The "steric" interaction of the geminal halogen atoms and the metal is also indicated by data obtained from the ^{19}F NMR spectra of perfluoroalkyl derivatives of mercury in solvents with different solvating capacities [74]. It has been shown that the constant for the spin–spin interaction between the mercury atom and the β-fluorine atom increases with increase of the solvating capacity of the solvent and that the opposite behaviour obtains for the fluorine atom in α-position. Evidently the donor solvent molecule competes with the α-fluorine atom in the interaction with the unfilled orbitals of the mercury atom, which leads to a decrease of the steric contribution to the quantity

$$J_{^{199}Hg-C-^{19}F}\,.$$

IV. SYNTHESES BASED ON DI(PERFLUORO-t-BUTYL)-MERCURY

It is well known that, in contrast to their non-fluorinated analogues, perfluoroalkylmercury compounds are extremely stable in relation to electrophiles. Their reactions with such reagents either proceed with difficulty or not at all [65]. This is shown, in particular, by the finding that the best method for their purification is distillation from concentrated sulphuric acid [62]. However, under the conditions of nucleophilic catalysis, the reactivity of perfluoroalkyl mercury compounds in reactions with electrophiles increases significantly, the most convenient catalysts being alkali metal fluorides [75],[76].

Evidently the fluoride ion is coordinated via its lone electron pairs to the mercury atom, but, in contrast to other halides, this coordination does not lead to the complete displacement of the perfluoroalkyl carbanion (and the decomposition of perfluoroalkylmercury), increasing merely the carbanionic character of the carbon atom linked to mercury; as a result, the complex formed in the process



$$F^{\ominus} + R_F{-}Hg{-}R_F \rightleftarrows [R_F{\cdots}Hg(F){-}R_F]^{\ominus}$$

enters into the reaction and not the free carbanion.

Thus reactions of di(perfluoroalkyl)mercury with various electrophiles become possible. For example, di(perfluoro-t-butyl)mercury and di(perfluoroisopropyl)mercury become desymmetrised by mercury(II) chloride in the presence of potassium fluoride:

$$(R_F)_2Hg + HgCl_2 \xrightarrow{KF} R_FHgCl\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

Potassium fluoride also catalyses the reactions of these mercury perfluoroalkyls with iodine:

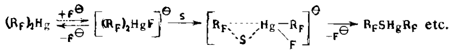
$$(R_F)_2Hg + I_2 \xrightarrow{KF} R_FI + HgI_2\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

It is noteworthy that di(perfluoro-t-butyl)mercury reacts with iodine in dimethylformamide also in the absence of a catalyst, probably due to the readily polarisability of iodine in a polar solvent; however, this reaction is much slower than in the presence of the fluoride ion.

When di(perfluoro-t-butyl)mercury and di(perfluoroisopropyl) mercury are heated with sulphur in dimethylformamide in the presence of potassium fluoride, mercury di(perfluoroalkyl)mercaptides are formed:

$$(R_F)_2Hg + S \xrightarrow{KF} (R_FS)_2Hg\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

The interaction of di(perfluoroalkyl)mercury with sulphur, catalysed by potassium fluoride, is remarkable in that it proceeds quite unambiguously—mercury perfluoroalkylmercaptides are the only reaction products. This finding suggests that the reaction with electrophiles proceeds within the limits of the complex $(R_F)_2Hg.KF$ without the involvement of the free carbanion:



Otherwise products of the oxidation of the perfluoroalkylmercaptide anion (di- and poly-sulphides) would have appeared in the reaction medium. Thus one may say that perfluoroalkylmercury compounds serve as a store of perfluoroalkylcarbanions and the experimental results obtained using the above method for their generation can differ from the results obtained in a fluoro-olefin–fluoride ion system.

In all the reactions enumerated above, di(perfluoro-t-butyl)mercury is much more reactive than di(perfluoroisopropyl)mercury. If one assumes that the catalytic activity of the fluoride ion is determined by its coordination to the mercury atom, the lower reactivity of perfluoroisopropylmercury can be accounted for not only by the destabilising effect of the fluorine atom in the α-position relative to the carbanionic centre but also by the competing intramolecular coordination of the mercury atom to the geminal fluorine atom.

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Radical-cation Mechanism of the Anodic Fluorination of Organic Compounds

I.N.Rozhkov

The current state of the problem of the electrochemical fluorination of organic compounds is surveyed, and the mechanism of the substitution of hydrogen by fluorine during anodic oxidation in anhydrous hydrogen fluoride and in aprotic organic solvents is discussed. Formation of a carbon-fluorine bond during oxidation at platinum in the latter solvents is shown to be due to reaction of an organic radical-cation with a fluoride anion present in the electrolyte. Arguments are given in support of a mechanism of electrochemical fluorination in hydrogen fluoride not involving oxidation of the fluoride anion. A list of 160 references is included.

CONTENTS

I. INTRODUCTION

Electrochemical fluorination in anhydrous hydrogen fluoride is an important industrial method for obtaining perfluorinated organic compounds. This interesting process, devised by Simons more than twenty-five years ago[1,2], consists in the electrolysis at nickel electrodes of solution of organic compounds in anhydrous hydrogen fluoride. It is used to obtain completely fluorinated alkanes, carboxylic acids and their derivatives, ethers, tertiary amines, alkanesulphonyl fluorides, and other groups of organic compounds. The electrochemical production of organofluorine compounds possesses several advantages over other methods of fluorination. Firstly, it is a most economic and a comparatively safe process. Another attractive feature of the Simons method is that it yields perfluorinated products retaining the functional group of the original compound.

Although electrochemical fluorination is at first glance a simple and convenient method of preparation, it possesses many substantial disadvantages. This process usually results only in exhaustive fluorination of the organic molecule, and incompletely fluorinated products cannot be obtained. Electrochemical fluorination is accompanied by less degradation of the initial carbon framework of the molecule than in other methods, but this is still considerable. The yield of products retaining the original structure does not normally exceed 30%.

Since 1950 numerous attempts have been made to improve and modernise the Simons process. However, although more than 250 publications have appeared, the mechanism and the principal laws of electrochemical fluorination have remained until recently almost uninvestigated, owing to the extreme difficulty of working in anhydrous hydrogen fluoride[3-7]. In Dresdner's apt phrase[8] electrochemical fluorination is "... an art in many respects. The conditions of operation... ... are based on highly empirical considerations"

However, results have recently been obtained in Knunyants' laboratory that have drawn slightly aside the "curtain of secrecy" hiding the mechanism of this complicated reaction. The present Review will examine facts in support of a mechanism of anodic fluorination involving initial oxidation of the organic compounds.

II. FUNDAMENTAL IDEAS ON THE MECHANISM OF ELECTROCHEMICAL FLUORINATION IN ANHYDROUS HYDROGEN FLUORIDE

Several hypothetical mechanisms—(1) radical, (2) fluorination by higher fluorides of nickel, and (3) fluorination by complex nickel fluorides—have been suggested for electrochemical fluorination in hydrogen fluoride. The present Section is mainly confined to experimental results inconsistent with these hypothetical mechanisms, suggesting that anodic fluorination is quite different in character.

1. Radical Mechanism

According to this mechanism, suggested by Simons as early as 1950,[1] the first step is oxidation of a fluoride anion at the anode to the radical. The formation of perfluorinated organic compounds results from subsequent homolytic substitution of hydrogen atoms:

$$F^- \xrightarrow[\text{Ni}]{-e} F^\cdot \xrightarrow[-\text{HF}]{\text{RH}} R^\cdot \xrightarrow{F^\cdot} R{-}F\ .$$

Nagase[5] assumes that electrochemical fluorination is "an anodic reaction very definitely of free-radical type". Chang and Watanabe[9] consider that the molecular fluorine evolved is adsorbed on the nickel anode covered with a film of the difluoride. Fluorination takes place directly in hydrogen-fluoride solution at or below 20°C. The reason why only perfluorinated compounds are formed is that slightly fluorinated products are soluble in hydrogen fluoride, and therefore continue to be involved in the process. Completely fluorinated organic compounds, however, lose their basicity and become almost insoluble.

This is why only perfluorinated compounds are removed from the electrolyte, either as gaseous products or as heavy liquids separating out at the bottom of the cell.

The radical mechanism represented the first attempt—which proved to be greatly oversimplified—at explaining the results. A striking feature is the marked difference between the products obtained by electrochemical fluorination and those resulting from the action of elementary fluorine on organic compounds. It is incomprehensible, for example, why attempts to fluorinate molecular chlorine to the pentafluoride ClF_5 by the action of fluorine dissolved in hydrogen fluoride have been unsuccessful, whereas anodic fluorination gives a high yield of this product[10,11]. Such a radical mechanism leaves completely obscure also problems associated with the effect of the electrode material on the process: (i) nickel has proved the only suitable material for the anode[12]; (ii) even the brand of nickel and its crystalline structure influence the relative proportions of products of the fluorination of tertiary amines[13,14]; (iii) when new nickel electrodes are used, a peculiar, fairly long induction period is observed, during which perfluorinated products are not formed on passage of a current[4,13,14]; and (iv) fluorination is affected also by the material of the cathode, the use of soft iron instead of nickel lowering the yield of perfluorinated amines by two-thirds[15].

2. Fluorination by Higher Fluorides of Nickel

The fluorinating agents in this hypothetical mechanism are higher fluorides of nickel—NiF_3 and NiF_4—whose formation follows initial formation of nickel difluoride when nickel electrodes undergo anodic polarisation in hydrogen fluoride[16-19]. This is the reason for the induction period. An organic molecule present in solution then reacts with the modified surface of the anode. Such heterophase fluorination results in the appearance of perfluorinated compounds:

$$\begin{gathered}\mathrm{Ni-2e+2F^- \rightarrow NiF_2}\\ \mathrm{NiF_2-}n\mathrm{e}+n\mathrm{F^- \rightarrow NiF_{\mathit{n}+2}}\quad (n=1,\ 2)\\ \mathrm{RH+NiF_{\mathit{n}+2} \rightarrow R{-}F+HF+NiF_2}\quad .\end{gathered}$$

The formation of nickel difluoride in absolute hydrogen fluoride leads to very high ohmic polarisation[19]. Addition to the solvent of water (up to 2%) produces a marked decrease in the resistance of the cell, since the anodic coating becomes semiconducting. Water was regarded as necessary for stabilising species—NiOF and $NiOF_2$—containing the nickel atom in a higher state of oxidation. This concept was even used as basis for a tentative estimate[9] of the content of higher fluorides in the coating: their formation accounts for 0.1–1% of the current.

Nor does a mechanism of heterophase anodic fluorination of organic compounds by higher fluorides of nickel provide an acceptable explanation of many facts. Firstly, fluorination should be promoted by the introduction of additives such as cobalt into the nickel, since higher fluorides of cobalt are known[20] to be good fluorinating agents. However, such additions produce a marked deterioration in the electrochemical process, with increase in degradation and decrease in yield[21]. Furthermore, qualitative differences exist between the products of electrolysis and of fluorination by higher metal fluorides[3-5]. In particular, the electrochemical process is distinguished by preservation of the functional group of the initial compound, whereas fluorination by cobalt(III) fluoride involves detachment of functional groups from the organic molecule.

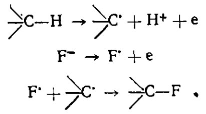
3. Fluorination by Complex Nickel Fluorides

In this mechanism, first suggested in 1960 by Burdon and Tatlow[4], highly conducting complexes of the organic compound with nickel fluorides—$(RH)_3NiF_6$ and $(RH)_2NiF_6$—are formed at the nickel electrode during electrolysis in hydrogen fluoride. Direct fluorination, i.e. replacement of hydrogen atoms in the organic molecule by fluorine atoms, occurs on decomposition of these complexes. Indirect evidence for this scheme was discovered later: (i) coloured anions—$[Ni^{3+}F_6]^{3-}$ and $[Ni^{4+}F_6]^{2-}$—were detected[22] in the anode layer during electrolysis of a solution of potassium fluoride in hydrogen fluoride; and (ii) potassium hexafluoronickelate, in anhydrous hydrogen fluoride at 0°C, reacts with xenon to form its difluoride[23].

Voitovich and Kazakov[24] regard this scheme as dubious, since the fluorinating effect of complex fluorides should be similar to the action of cobalt(III) fluoride. Electrochemical processes should not yield perfluorinated products with a retained functional group. In their opinion the primary act of the electrochemical process must be formation of nickel difluoride, which, in the presence of fluoride ions and e.g. a protonated tertiary amine, is oxidised electrochemically to a complex of type (I), sparingly soluble in hydrogen fluoride:

$$\begin{gathered}\mathrm{R_3N+HF \rightarrow R_3NH^+ + F^-}\\ n\mathrm{(R_3NH)^+ + NiF_2 + 2F^- \rightarrow (R_3NH)_{\mathit{n}}\,NiF_{\mathit{n}+4} + 2e}\quad .\\ \text{(I)}\end{gathered}$$

The compound R_3N, having entered the complex, is then oxidised electrochemically at carbon–hydrogen bonds to form radicals, able to recombine with fluorine radicals appearing at the anode from the discharge of fluoride anions:

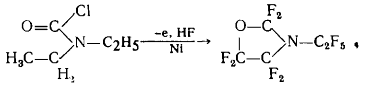


The completely (or almost completely) fluorinated amine loses its basicity, with the result that the complex breaks down:

$$\begin{gathered}\mathrm{[(R_F)_3\,NH]_{\mathit{n}}\,NiF_{\mathit{n}+4} \rightarrow \mathit{n}\,(R_F)_3\,N + \mathit{n}\,HF + NiF_4}\\ \mathrm{NiF_4 \rightarrow NiF_2 + 2F^{\cdot}}\quad .\end{gathered}$$

The main direction of electrochemical fluorination—substitution of hydrogen in the organic molecule by fluorine—is attributed to adsorption of the organic compound on the anode during formation of the complex, with a resultant weakening of carbon–hydrogen bonds. As a consequence, these bonds are preferentially attacked by the fluorine radical, while the carbon–carbon bonds are considerably less affected. In the case of substances that possess no basicity, fluorination takes place on the surface of complex inorganic fluorides such as K_2NiF_6. On such a surface electrochemical oxidation of carbon–carbon bonds predominates, which leads to considerable degradation of the initial molecule.

In spite of the great attractiveness of this mechanism, however, it cannot explain several facts. Firstly, if a complex is formed, why a large excess of the organic compound should favour the formation of incompletely fluorinated products is obscure[25,26]. Secondly, if anodic fluorination is a radical process, the introduction of acceptor substituents into the initial organic molecule should hinder radical fluorination and yield only partly fluorinated compounds; yet perfluorinated products exclusively were isolated from the electrochemical fluorination of sulphones[27,28] and nitroalkanes[29] in hydrogen fluoride. Thirdly, it is incomprehensible with such a reaction scheme why fragmentation of the organic molecule increases when the current density is lowered[8,30]. Finally, it is difficult to explain the cyclisations[31,32] and isomerisations[33,34] typical of electrochemical fluorination at nickel in hydrogen fluoride:

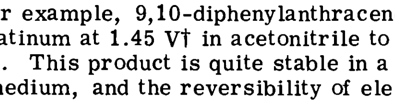


Replacement of hydrogen by fluorine atoms in the anodic fluorination of *N*-alkylpiperidines is accompanied by a peculiar isomerisation of the carbon skeleton. Fluorination of the isopropyl, isobutyl, and isopentyl derivatives gives mixtures of perfluoroalkylpiperidines having branched and unbranched alkyl chains. The content of the straight-chain isomer increases with chain length, to reach 75–90% with the isopentyl compound. Formation of perfluorinated products having an iso-structure is not observed on the fluorination of amines containing n-alkyl substituents[34].

III. *ECE* MECHANISM OF ANODIC FLUORINATION IN APROTIC SOLVENTS

A characteristic feature of the above hypothetical mechanisms of electrochemical fluorination in hydrogen fluoride is a homolytic reaction involving the fluorine radical. It was supposed[7] that "the only anions present in solution are fluoride ions, which excludes the possible occurrence of processes other than discharge of the fluoride anion". The radical type of fluorination can obviously take place at an anode potential adequate for oxidation of the fluoride ion, i.e. above 2.85 V.[35–39].

Many classes of organic compounds, however, are oxidised at considerably lower anodic potentials[40]. This difference in oxidation potentials has revealed a possible new route for the introduction of fluorine into an organic molecule in an electrochemical process. In 1970 Knunyants et al.[41–43] found that anodic oxidation can be used to generate at a platinum anode an organic cation that will then react with a fluoride anion in solution to form a carbon–fluorine bond. This process is applicable to the anodic fluorination of many classes of organic compounds having oxidation potentials below 2.85 V: e.g.



This mthod for the anodic fluorination of organic compounds opened up wide possibilities for studying the mechanism, since it enabled anhydrous hydrogen fluoride and nickel to be dispensed with as solvent and as the only suitable material for the anode. Anodic substitution of hydrogen by fluorine in an organic molecule occurred smoothly on platinum in solutions of fluorides in aprotic solvents. For example, 9,10-diphenylanthracene is oxidised on platinum at 1.45 V† in acetonitrile to form a radical-cation. This product is quite stable in a non-nucleophilic medium, and the reversibility of electron transfer could be demonstrated by cyclic voltammetry with a triangular pulse[44–46]. An oscillopolarogram obtained during anodic polarisation exhibits a peak representing the oxidation of diphenylanthracene to a radical-cation (Fig. 1*a*, curve *BA*$_1$*M*), which on reverse cathodic scanning acquires an electron and is reduced to the original compound (curve *MC*$_1$*D*). Anodic and cathodic peaks *A*$_1$ and *C*$_1$ have the same height[44].

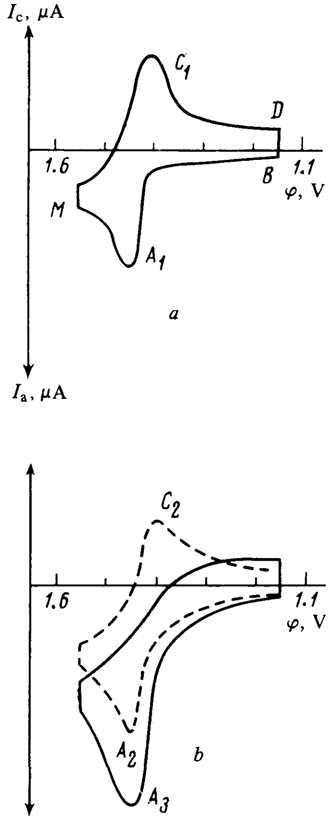


Figure 1. Cyclic voltammetry of 9,10-diphenylanthracene: *a*) non-nucleophilic medium (CH_3CN, $(C_2H_5)_4NClO_4$); *b*) as (*a*) in presence of the fluoride anion—$(C_2H_5)_4NF$.

Extremely significant changes are observed when tetraethylammonium fluoride is added to this solution[47–49] (Fig. 1*b*): the anodic peak *A*$_3$ expands at the same potential and now corresponds to a two-electron oxidation; and the transfer of electrons to the anode becomes irreversible, with no cathodic peak present on reverse scanning. Reaction of the radical-cation with the fluoride anion has a large rate constant, but lowering the temperature to −30°C and increasing a hundredfold the rate of scanning nevertheless enables a cathodic peak *C*$_2$ to be registered.

The picture obtained agrees excellently with the theory of the so called *ECE* mechanism (where *C* and *E* denote chemical and electrochemical stages respectively)[50–53]. It had been shown with 9,10-diphenylanthracene as example[54–56] that the addition of pyridine converted the

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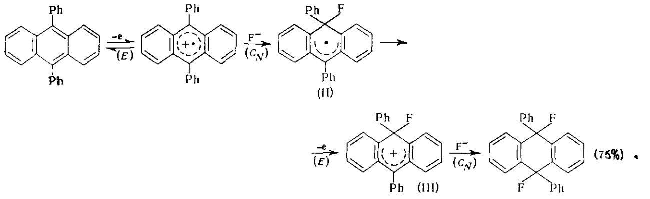
† Potentials in this Review are given relative to the normal hydrogen electrode.

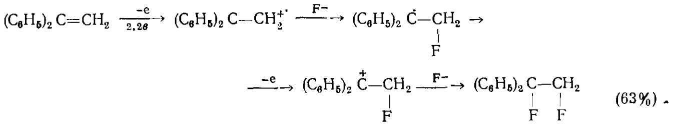
original one-electron mechanism of oxidation into a two-electron mechanism. Similarly in the oxidation of 9-phenylanthracene[57] the anodic peak in the oscillopolarogram increased greatly in the presence of water. The preparative electrolysis of 9,10-diphenylanthracene in the presence of the fluoride ion (tetraethylammonium fluoride in acetonitrile at 1.45 V) gives a 75% yield of 9,10-difluorodihydro-9,10-diphenylanthracene[58]. The same results are obtained when diphenylanthracene is electrolysed at 1.90 V [59] (corresponding to the formation potential of the bication[46]) in a solution of $(CH_3)_4NH_2F_3$ in acetonitrile. Thus in this case an EC_NEC_N mechanism operates (where C_N denotes a stage of nucleophilic chemical reaction)[56,60–62]:



A condition for such a mechanism is that the potential for oxidation of the intermediate radical (II) to the cation (III) should be lower than or equal to the oxidation potential of the initial molecule, a condition that is satisfied by aromatic compounds[63].

The main conclusion that follows from the experiment with 9,10-diphenylanthracene is that formation of a carbon–fluorine bond takes place at potentials considerably below the oxidation potential of the fluoride anion.

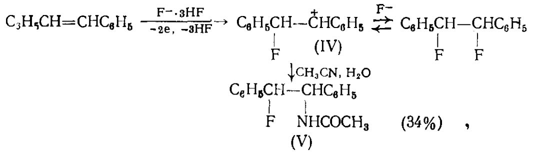
An EC_NEC_N mechanism probably operates also in the anodic oxidation of alkenes[64,65]. In the presence of the fluoride anion their oxidation at platinum leads in several cases to addition of two fluorine atoms at the double bond:



$$(C_6H_5)_2C{=}CH_2 \xrightarrow[2,26]{-e} (C_6H_5)_2C{-}CH_2^{+\cdot} \xrightarrow{F^-} (C_6H_5)_2\dot{C}{-}\underset{\displaystyle F}{\underset{|}{CH_2}} \rightarrow$$

$$\xrightarrow{-e} (C_6H_5)_2\underset{\displaystyle F}{\underset{|}{\overset{+}{C}}}{-}CH_2 \xrightarrow{F^-} (C_6H_5)_2\underset{\displaystyle F}{\underset{|}{C}}{-}\underset{\displaystyle F}{\underset{|}{CH_2}} \quad (63\%) .$$

With stilbene use as electrolyte of a solution of tetraethylammonium fluoride–3-(hydrogen fluoride) in acetonitrile results in fluoroacetamidation, which is explained by the great mobility of the benzyl fluorine atom in acid medium:



$$C_3H_5CH{=}CHC_6H_5 \xrightarrow[-2e,\ -3HF]{F^-\cdot 3HF} \underset{\displaystyle F}{\underset{|}{C_6H_5CH}}{-}\overset{+}{C}HC_6H_5 \overset{F^-}{\rightleftarrows} \underset{\displaystyle F}{\underset{|}{C_6H_5CH}}{-}\underset{\displaystyle F}{\underset{|}{CHC_6H_5}}$$

$$(IV)$$

$$\downarrow CH_3CN,\ H_2O$$

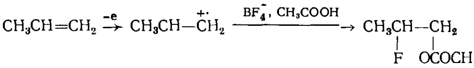
$$\underset{\displaystyle F}{\underset{|}{C_6H_5CH}}{-}\underset{\displaystyle NHCOCH_3}{\underset{|}{CHC_6H_5}} \quad (34\%) ,$$

$$(V)$$

Addition of a fluoride anion to the cation (IV) in acid medium is reversible, so that (IV) undergoes an irreversible Ritter reaction with acetonitrile. Further substitution of the fluorine atom in (V) by an acetamido-group does not occur owing to its insolubility in acetonitrile. Schmidt[67,68] had earlier reported the addition of two fluorine atoms in the anodic oxidation of stilbene and cyclohexene in an acetonitrile solution of silver fluoride. However, these results could not be reproduced[66], since such solutions are non-conducting.

Acetamidation takes place in the anodic oxidation not only of alkenes but also of alkanes and alkylbenzenes[69]. To avoid this reaction other solvents, in particular dichloromethane, are usually employed in the electrolysis[70,71].

It has recently been found that the tetrafluoroborate anion may also be a source of the fluoride anion in the anodic fluorination of alkenes. Thus fluorinated acetates are formed in the anodic oxidation of alkenes in acetic acid with ammonium tetrafluoroborate as supporting electrolyte[72]:



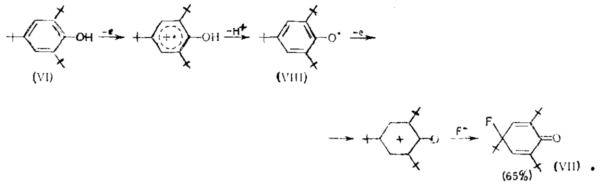
$$CH_3CH{=}CH_2 \xrightarrow{-e} CH_3CH{-}\overset{+\cdot}{C}H_2 \xrightarrow{BF_4^-,\ CH_3COOH} \underset{\displaystyle F}{\underset{|}{CH_3CH}}{-}\underset{\displaystyle OCOCH_3}{\underset{|}{CH_2}} .$$

Substitution of hydrogen by fluorine (also at potentials considerably below the oxidation potential of the fluoride anion) is also possible in the anodic oxidation of organic compounds at platinum in the presence of the fluoride anion in acetonitrile. This process has been observed with aromatic compounds (below) even in cases[73,75] in which the intermediate radical-cation of the organic molecule is capable of rapid elimination of a proton under the influence of a base. For example, the oxidation of triphenylmethane, obviously by an EC_bEC_N mechanism, gives a high yield of triphenylmethyl fluoride[73]:

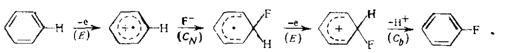
$$(C_6H_5)_3CH \underset{(E)}{\xrightarrow[1.8\ V]{-e}} (C_6H_5)_3\overset{+\cdot}{C}H \underset{(C_b)}{\xrightarrow[-3HF]{F^-}} (C_6H_5)_3\dot{C} \xrightarrow[(E)]{-e}$$

$$\rightarrow (C_6H_5)_3\overset{+}{C} \xrightarrow[(C_N)]{F^-} (C_6H_5)_3C{-}F \quad (80\%) .$$

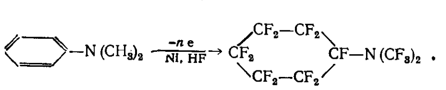
Such rapid elimination of a proton (stage C_b) is extremely characteristic of radical-cations not only of alkylbenzenes but also of phenols[40,74]. The oxidation of tri-t-butylphenol (VI) by the above mechanism yields the "quinofluoride" (VII).[75] The corresponding formation of a chlorocyclohexadienone had previously been observed in the oxidation of (VI) in the presence of the chloride anion[76,77]. The light blue stable radical (VIII) was recorded[78] in the anodic oxidation:



A distinguishing feature of the anodic oxidation of aromatic compounds in the presence of the fluoride anion is the partial replacement of hydrogen by fluorine while the aromatic structure is preserved, which involves an EC_NEC_b mechanism of fluorination. In the oxidation of benzene at platinum in acetonitrile, for example, fluorobenzene is obtained in 40% yield[79]:



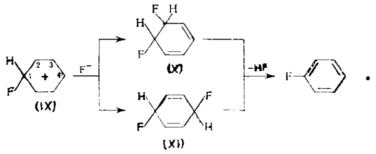
Yet the Simons method of fluorinating aromatic compounds (at nickel in anhydrous hydrogen fluoride) usually occurs exhaustively to give derivatives of perfluorocyclohexane[5–7] and in some cases resinous products[2,80,81]:



Oxidation by cyclic voltammetry at platinum[82] shows that at 2.63 V benzene forms a radical-cation, which rapidly eliminates a proton, after which polymerisation takes place and a polyphenylene film appears on the anode:

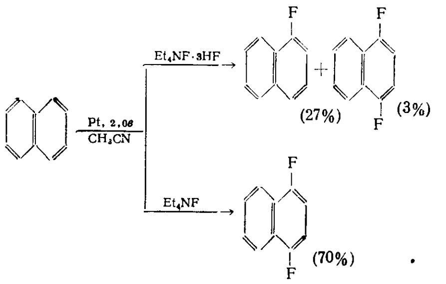
$$C_6H_6 \xrightarrow{-e} C_6H_6^{+\cdot} \xrightarrow{-H^+} C_6H_5^{\cdot} \rightarrow \text{Biphenyl + Polyphenylenes} .$$

In the presence of the fluoride anion the radical-cation is stabilised by nucleophilic attack. The above EC_NEC_b scheme of formation of fluorobenzene may be rather more complicated: the arenonium ion (IX) may add a second fluoride anion; this nucleophilic attack on (IX) should follow at the 2- and 4-carbon atoms with formation of the difluorocyclohexadienes (X) and (XI):

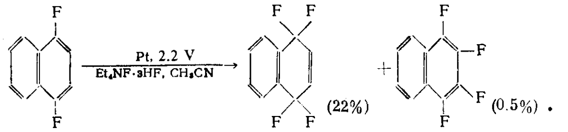


Calculations by the INDO method[83] using a TOREAMOR programme[84,85] show that the greatest positive charge is concentrated on these carbon atoms in the cation (IX): values for $C_{(1)}$–$C_{(4)}$ are respectively +0.254, +0.140, −0.012, and +0.275.

The anodic fluorination of naphthalene on platinum yields 1-fluoronaphthalene and 1,4-difluoronaphthalene depending on the conditions[41,42]:

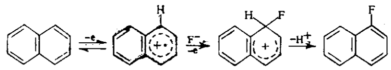


Prolonged electrolysis results in further fluorination to 1,1,4,4-tetrafluorodihydronaphthalene and traces of 1,2,3,4-tetrafluoronaphthalene:

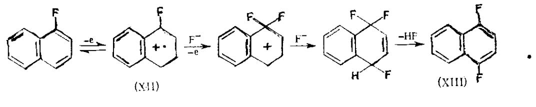


A striking feature is the sharp orientation of the substitution of hydrogen by fluorine: initially only 1-fluoronaphthalene is formed, after which 1,4-difluoronaphthalene appears. Yet anodic cyanation[86] and acetoxylation[87–89] yield mixtures of the 1- and 2-substituted naphthalenes. It must be emphasised that, in the anodic fluorination of naphthalene, a carbon–fluorine bond can be formed only by reaction with a fluoride anion. Radical fluorination by F· is excluded, for the anodic potential is only 2.0 V. Cyanation and acetoxylation, however, may be radical processes, since the oxidation potentials are 0.73 and 1.83 V for the cyanide[86] and acetate[90] ions respectively. Occurrence of a radical process in anodic acetoxylation is confirmed by the formation of methylnaphthalenes[88], which indicates that the acetate anion is oxidised to a radical, subsequently decarboxylated with formation of a methyl radical.

In the anodic fluorination of naphthalene (when homolytic substitution is exluded) it may be supposed that the orientation of nucleophilic attack by the fluoride anion will be determined by the distribution of positive charge in the radical-cation[42]. Inspection of Table 1 shows that, when anodic fluorination occurs on platinum, replacement of hydrogen by fluorine takes place at the carbon atom bearing the highest total positive charge in the radical-cation. Thus the initial nucleophilic attack

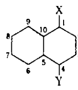


is governed by the distribution of positive charge density. The positive charges at positions 1 and 4 in the radical-cation of 1-fluoronaphthalene are respectively 0.392 and 0.120. Nucleophilic attack is therefore extremely probable at position 1, with subsequent stabilisation of the cation by addition of a second fluoride anion and detachment of hydrogen fluoride:



This direction of attack on the radical-cation (XII) is confirmed indirectly by the formation of tetrafluorodihydronaphthalene on the anodic fluorination of (XIII).

Table 1. Distribution of charge in the radical-cation.



X	Y	Total charge on atom										Calcn.	Ref.
		1	2	3	4	5	6	7	8	9	10		
H	H	0.181	0.069	0.069	0.181	—	—	—	—	—	—	MOX	42
H	H	0.104	0.048	0.048	0.104	0.010	—	—	—	—	0.010	CNDO	91
F	H	0.392	0.004	0.080	0.120	0.032	0.101	0.066	0.067	0.117	−0.037	INDO	48
F	H	0.338	0.001	0.053	0.104	0.027	0.079	0.044	0.049	0.091	−0.020	CNDO	91
F	H	0.242	0.049	0.054	0.163	—	0.122	0.042	0.056	0.112	—	MOX	42
F	F	0.380	0.017	0.017	0.380	−0.016	0.099	0.066	0.066	0.099	−0.016	INDO	48
F	F	0.331	0.006	0.006	0.331	−0.006	0.049	0.047	0.047	0.049	−0.006	CNDO	91

All the above *ECE* schemes of anodic fluorination on platinum consist in the successive transfer of two electrons separated by an intermediate chemical stage (reaction with a nucleophile or elimination of a proton). In some cases anodic fluorination may involve the transfer of only one electron to the anode. An example is the anodic oxidation of tetra-alkylsilanes, which in the presence of fluoride ions leads to replacement of an alkyl group by fluorine[92]:

$$R_4Si \xrightarrow[F^-]{-e} R_4SiF^\cdot \xrightarrow{-R^\cdot} R_3Si{-}F \quad (50\text{–}80\%) \ .$$

In concluding this Section we must examine a recent paper by Eberson[93], who concludes, on the basis of certain experimental results[94–96] and a theoretical survey, that the interaction of an aromatic radical-cation with a halide anion X^- involves merely the transfer of an electron. In his opinion nucleophilic attack by halide anions is forbidden by the Dewar–Zimmerman rules[97]. Assuming that attack by a nucleophile takes place along the normal to the plane of the ring passing through the middle of a carbon–carbon bond, Eberson distinguishes between suprafacial and antarafacial attack (in which the nucleophile orbital interacting with the π-system of the ring is respectively symmetric and antisymmetric—(*a*) and (*b*) in Fig. 2). The transition state of the seven-membered ring corresponds respectively to Hückel and anti-Hückel systems. With eight electrons (systems having an odd number of electrons are treated as containing a fictitious extra electron) the second transition state is aromatic and corresponds to an allowed process, whereas the first is antiaromatic and hence forbidden by the Dewar–Zimmerman rules. A vulnerable point in Eberson's argument is[58] the choice of nucleophile orbital interacting with the radical-cation. He considers only the p_z orbital of halogens. Nevertheless, estimates of the overlap integrals for fluoride and chloride ions indicate close similarity of interaction of the p_z and p_x orbitals of the halogen with the p_z orbitals of carbon atoms[58]. Thus, although suprafacial interaction (Fig. 2*a*) is indeed prohibited by the Dewar–Zimmerman rules, nucleophilic attack on aromatic radical-cations by halide anions may result from the antarafacial interaction, disregarded by Eberson, of a lone pair of the halide ions located in a p_x orbital (Fig. 2*b*).

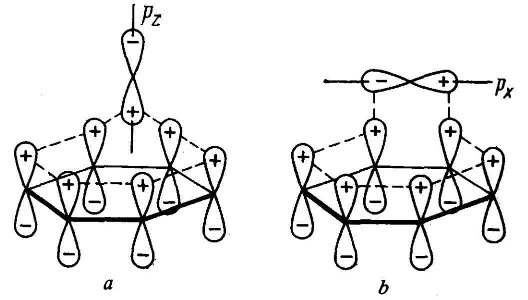
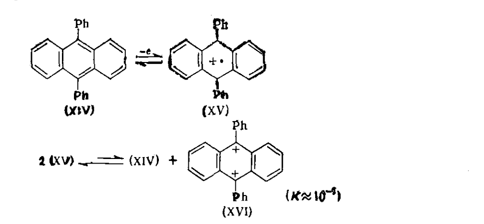


Figure 2. Arrangement of orbitals of transition state in nucleophilic attack on the radical-cation of an aromatic compound: *a*) suprafacial attack; *b*) antarafacial attack.

Nucleophilic attack by halide anions on aromatic radical-cations is supported by several experimental facts. (1) Millington[98] showed that high yields of 1-bromonaphthalene are formed by the anodic oxidation of naphthalene in the presence of bromide ions. (2) The radical-cation of diphenylanthracene reacts with the chloride anion to form chlorinated products of undetermined structure[99]. (3) In the presence of the chloride ion the chemical oxidation of anisole and naphthalene[100,101] by sodium peroxodisulphate to the radical-cations yields the corresponding monochlorinated aromatic compounds. (4) Nucleophilic attack on aromatic radical-cations by the fluoride anion probably occurs under the influence of xenon difluoride in hydrogen fluoride[102,103]. (5) Burdon[91] gives several forcible arguments for nucleophilic attack by the fluoride ion on aromatic radical-cations during fluorination with cobalt(III) fluoride. (6) In many cases the anodic oxidation of aromatic compounds in the presence of fluoride anions yields compounds containing fluorine.

Nucleophilic reaction between the fluoride ion and a radical-cation is convincingly confirmed by the kinetics of the cyclic voltammetry of diphenylanthracene (XIV) in the presence of the fluoride anion[58]:



$$(XVI) + F^- \rightarrow \text{Products} \quad .$$

Other possible reaction paths are rejected. Thus disproportionation of the radical-cation[104-106] is unreal, since extraordinarily high rate constants must then be assumed for reaction of the fluoride ion with the bication (XVI). Furthermore, the kinetics of the reaction of (XV) with pyridine shows a first order with respect to diphenylanthracene, which excludes disproportionation of (XV).[107,108] The high oxidation potential of the fluoride ion excludes another possible path, which would have "avoided" nucleophilic attack by the ion on the radical-cation (XV)

$$(XIV) \underset{}{\overset{-e}{\rightleftharpoons}} (XV)$$

$$(XV) + F^- \not\rightarrow (XIV) + F^\bullet$$

$$(XIV) + F^\bullet \longrightarrow \text{Products} \quad .$$

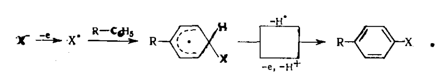
IV. ORIENTATION OF NUCLEOPHILIC ATTACK IN RADICAL-CATIONS OF AROMATIC COMPOUNDS

Results obtained during recent years showed convincingly that the electrochemical oxidation of aromatic compounds in non-nucleophilic media usually involves the transfer of a single electron to the anode with formation of a radical-cation[109]. In a nucleophilic medium the oxidation becomes a two-electron process: an *ECE* mechanism of anodic substitution operates (acetoxylation, cyanation, methoxylation)[110,111]. The exceptional character of anodic fluorination by an *ECE* mechanism lies in the impossibility of a parallel homolytic process (the anodic potential is insufficient for formation of the fluorine radical). Acetoxylation, cyanation, and methoxylation, however, occur at anode potentials sufficient for oxidation of the corresponding anions to radicals.

The formation of substitution products in an anodic process can be regarded as the result of reactions occurring by the following mechanisms.

(*a*) *ECE* Mechanism. It is assumed in this case that the orientation of nucleophilic attack and hence the relative proportions of isomers are determined by the distribution of positive charge density in the radical-cation of the aromatic compound[40,42,47,94,112].

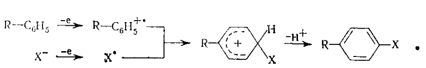
(*b*) Radical mechanism. An analogy with homolytic aromatic substitution should be observed:



The same products will result from initial oxidation of the aromatic substrate followed by a redox reaction of the radical-cation with the anion X⁻:

$$R-H \overset{-e}{\rightleftharpoons} R-H^{+\bullet} \xrightarrow{X^-} R-H + X^\bullet \quad .$$

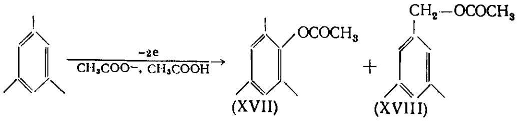
(*c*) Parallel oxidation. The aromatic molecule is oxidised to the radical-cation and the anion X^- is oxidised simultaneously. The orientation of substitution would then be determined by the distribution of density of the lone electron in the radical-cation:



It is evident that processes by all three mechanisms (*a*)-(*c*) involve the transfer of two electrons to the anode. Thus microcoulometry is uninformative in these cases. Several authors adduce the results of polarisation measurements, which register the anodic depolarisation effect on addition of an aromatic compound, as the main argument in support of an *ECE* mechanism for cyanation or acetoxylation. The weakness of such arguments has recently been pointed out by Mirkind[111].

In the Reviewer's opinion anodic acetoxylation and cyanation can take place by *ECE* and radical mechanisms simultaneously, the relative importance of the latter depending on the conditions[23]. The distribution of reaction products is greatly affected by the state of the anode surface and by adsorption. Very significant results have been obtained for the effect of adsorption in the acetoxylation of anisole on platinum[113]: whereas in the absence of any additive the ratio of the *o*- and *p*-methoxyphenyl acetates formed is 2.2, the addition of small quantities of napththalene to the electrolyte produces a sharp decrease in the proportion of the *ortho*-isomer, and the ratio falls to unity. Acetoxylation probably occurs mainly by a radical mechanism in the absence of additives: the ratio of the products agrees well with the orientation of attack in the homolytic substitution of hydrogen in anisole. Addition of naphthalene, which is strongly adsorbed on platinum, blocks the anode surface, which hinders oxidation of the acetate anion. Only strong electron donors such as anisole can compete with naphthalene for a place on the surface of the platinum anode. In this case anisole is oxidised to the radical-cation, its acetoxylation takes place mainly by an *ECE* mechanism, and the *ortho/para* ratio agrees well with the results of anodic fluorination.

The influence of the anode material on the relative proportions of products of the acetoxylation of mesitylene



is also extremely significant[114]. The ratio of products of acetoxylation in the ring and in the side-chain (XVII)/(XVIII) has the values 4.4 and 23 on platinum and on graphite respectively. Adsorption of the acetate on platinum is large, and it undergoes oxidation with subsequent radical reaction in the side-chain. On graphite, however, the adsorption of acetate is small[7], so that the main process is the adsorption of mesitylene, its oxidation to the radical-cation, and subsequent reaction with the acetate ion. In this case acetoxylation occurs almost exclusively in the ring. The composition of the electrolyte also influences the ratio of the products of the acetoxylation of mesitylene[115].

We shall now consider the orientation of the substitution of hydrogen by fluorine in the anodic fluorination of aromatic compounds.

1. Donor Substituents

The special feature of the anodic fluorination of aromatic compounds by the *ECEC* mechanism—the impossibility of parallel homolytic reactions—is clearly revealed by a comparison with other anodic aromatic substitutions. Table 2 summarises data on the effect of substituents on the orientation of anodic substitution in aromatic compounds. It includes results for certain homolytic reactions and "oxidative" substitutions in the aromatic ring, to which is attributed a mechanism with intermediate formation of radical-cations and subsequent nucleophilic attack. Analysis of all these results leads to the following conclusions.

Table 2. Proportions of products in the substitutions $R.C_6H_5 \rightarrow R.C_6H_4.X + X.C_6H_5$.

No.	R	Anodic reaction			Chemical reaction	X	Isomers, %				Ref.
		φ, V	anion	solvent*			XC_6H_5	*o*-	*m*-	*p*-	
1	CH_3	2.63	F·3HF	A		F	—	43	—	57	47, 116
2	»	—	CH_3COO	Y		CH_3COO	—	48	11	41	117
3	»	2.13	»	Y		»	—	43	11	46	89
4	»	—	CN	M		CN	—	40	8	52	118
5	»	—	CN	A		CN	—	32	2	65	86
6	»				$Na_2S_2O_8+LiCl+CuCl_2$	Cl	—	58	4	38	100, 101
7	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	—	57	15	28	119
8	»				F_2, CF_3COOH	F	—	67	15	18	120
9	»				$(CH_3COO)_2$	CH_3	—	57	26	17	121
10	C_2H_5	2.13	CH_3COO	Y		CH_3COO	—	44	10	46	89
11	»		»	Y		»	—	48	12	40	88
12	i-C_2H_7	2.30	F·3HF	A		F	2	48	—	50	122, 123
13	»	2.13	CH_3COO	Y		CH_3COO	—	44	17	39	89
14	t-C_4H_9	2.20	F·3HF	A		F	17	17	—	66	122, 123
15	t-C_4H_9		CH_3COO	Y		CH_3COO	—	27	25	48	88
16	»	2.13	»	Y		»	—	35	22	43	89
17	»				$(C_6H_5COO)_2$	C_6H_5	—	24	49	27	121
18	OCH_3	1.85	F·3HF	A		F	2	43	—	55	47, 116
19	»	—	CH_3COO	Y		CH_3COO	—	70	2	28	117
20	»	1.73	»	Y		»	—	86	—	14	87
21	»	»	»	Y		»	—	67	4	29	89
22	»	2.03	»	Y		»	—	68	—	32	113
23**	»	»	»	Y		»	—	50	—	50	113
24	»	—	CN	A		CN	—	53	—	47	118
25	»	—	CN	A		CN	—	51	—	49	86
26	»	1.98	NO_2	A		NO_2	—	***	—	***	124
27	»				XeF_2, HF	F	—	52	5	42	125
28	»				$Ag_2S_2O_2+CH_3COOH$	CH_3COO	—	68	1	31	126
29	»				$(CH_3COO)_2$	CH_3	—	74	15	11	121
30	OC_2H_5	1.85	F·3HF	A		F	—	40	—	60	47, 116
31	F	2.63	F·3HF	A		F	—	—	—	99	127
32	»	2.19	CH_3COO	Y		CH_3COO	—	34	8	58	89
33	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	—	33	22	45	119
34	»				XeF_2, HF	F	—	30	—	70	102
35	F				$(CH_3COO)_2$	CH_3	—	57	37	6	121
36	Cl	2.63	F·3HF	A		F	16	25	—	61	123, 127
37	»	2.19	CH_3COO	Y		CH_3COO	—	37	6	58	89
38	»		CN	A		CN	—	50	—	50	118
39	»				$Co(OCOCH_3)_3$	CH_3COO	10	30	—	60	128
40	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	—	54	13	33	119
41	»				$Na_2S_2O_8+LiCl+CuCl_2$	Cl	—	40	5	55	101
42	»				$(CH_3COO)_2$	CH_3	—	62	28	10	121
43	Br	2.63	F·3HF	A		F	18	21	—	61	127
44	»	2.23	CH_3COO	Y		CH_3COO	—	30	4	66	89
45	»				$(CH_3COO)_2$	CH_3	—	62	28	10	121

*Solvents: A = acetonitrile; M = methanol; Y = acetic acid.

** Electrolysis in the presence of naphthalene.

*** Isomers detected in the electrolysis products.

1. In no case of the anodic fluorination of an aromatic compound containing a donor substituent has the formation of a *m*-fluoro-isomer been recorded (Table 2, No. 1, 12, 14, 18, 30, 31, 36, and 43). In contrast, anodic acetoxylation and cyanation lead in most cases to a considerable

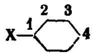
quantity of the *meta*-isomer among the reaction products (No. 2–4, 10, 11, 13, 15, 17, 21, 32, 37, and 44). "Oxidative" substitutions also yield the *meta*-isomer (No. 6, 7, 27, 33, 40, and 41). The *meta*-isomer is formed in all cases of homolytic substitution (No. 8, 9, 17, 29, 35, 42, and 45).

2. The anodic fluorination of aromatic compounds containing donor substituents (t-butyl, methoxyl, ethoxyl, chlorine, bromine) usually yields mainly the *para*-isomer, whose ratio to the *ortho*-isomer lies in the range 2–3. With methyl and isopropyl substituents the ratio is unity. Nevertheless, the *ortho*-isomer usually predominates in other anodic substitutions and in "oxidative" substitutions (Table 2, No. 2, 6, 7, 11, 13, 19–21, 24, 27, and 28). This isomer predominates also in homolytic substitutions (No. 8, 9, 17, 29, 35, 42, and 45).

3. A distinguishing feature of anodic fluorination is *ipso*-attack, leading to the replacement of isopropyl, t-butyl, and methoxyl groups, as well as chlorine and bromine atoms (Table 2, No. 12, 14, 18, 36, and 43).

4. Fluorobenzene exhibits a marked difference in orientation of substitution, with exclusive formation of the *para*-isomer.

Table 3. Distribution of total charge density in the radical-cation



X	Calcn.*	Total charge on atom				Ref.
		1	2	3	4	
CH_3	1	0.206	0.060	0.052	0.188	122, 123
	2	0.130	0.073	0.076	0.064	103
$C(CH_3)_3$	1	0.178	0.051	0.048	0.168	122, 123
$O—CH_3$	1	0.185	0.037	0.045	0.095	»
$O—CF_3$	1	0.299	0.032	0.057	0.145	»
$S—CH_3$	1	0.074	0.046	0.048	0.063	»
$S—CF_3$	1	0.081	0.050	0.049	0.074	»
F	1	0.430	0.018	0.069	0.170	»
	2	0.276	0.131	0.103	0.093	103
	3	0.380	0.015	0.045	0.158	91
Cl	1	0.110	0.053	0.055	0.072	122, 123

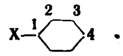
* Methods of calculation: 1) INDO;[122,123] 2) MWH;[103] 3) CNDO/2.[91]

We shall now compare the data in Table 2 with calculated positive charge densities (Tables 3 and 4) and spin densities (Table 5) for the radical-cations of aromatic compounds. This leads to the following detailed conclusions on the mechanism of anodic fluorination and the orientation of nucleophilic attack in such radical-cations.

(1) Nucleophilic attack by a fluoride anion is governed by the density distribution of positive charge in the radical-cation. Only the π-component of the charge does not determine the position of attack. In the radical-cations of anisole and chlorobenzene, for example, the π-component of the charge at position 1 is respectively 0.047 and –0.135. Yet the corresponding total charges at this position are +0.185 and +0.110. Attack at position 1 occurs both in anisole and in chlorobenzene, since the product was fluorobenzene, resulting from replacement of the methoxy-group and the chlorine atom.

(2) The density distribution of the unpaired electron usually correlates well with the positive charge distribution in the radical-cation (the atom bearing the highest positive charge possesses also the greatest spin density). Nevertheless, the density distribution of the unpaired electron has no effect on the orientation of attack in anodic fluorination. For example, the distribution of spin density cannot explain the *ipso*-attack and simultaneous absence of the *meta*-isomer in the case of anisole.

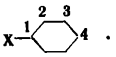
Table 4. Distribution of density of π-component of charge in the radical-cation



X	Calcn.*	π-Component of charge on atom			
		1	2	3	4
CH_3	1	0.301	0.076	0.067	0.263
»	2	0.308	0.083	0.055	0.266
$C(CH_3)_3$	1	0.286	0.074	0.057	0.243
$O—CH_3$	1	–0.047	0.049	0.026	0.124
$O—CF_3$	1	0.117	0.067	0.050	0.210
$S—CH_3$	1	–0.109	0.017	0.018	0.071
$S—CF_3$	1	–0.108	0.031	0.020	0.090
F	1	0.233	0.065	0.070	0.257
»	2	0.341	0.081	0.068	0.299
Cl	1	–0.135	0.031	0.019	0.088
»	2	0.323	0.084	0.071	0.306
Br	2	0.304	0.084	0.067	0.294

* Methods of calculation: 1) INDO; 2) MOX.

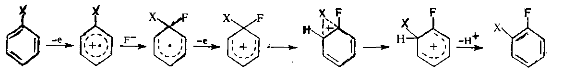
Table 5. Distribution of spin density in the radical-cation



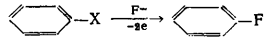
X	Calcn.*	Total spin density on atom			
		1	2	3	4
CH_3	1	–0.340	–0.115	+0.029	–0.410
»	2*a*	0.308	0.093	0.070	0.310
»	3	0.339	0.081	0.033	0.355
$O—CH_3$	1	+0.077	–0.166	+0.103	–0.205
»	2*b*	0.258	0.122	0.048	0.282
$O—CF_3$	1	–0.129	–0.166	+0.087	–0.331
$S—CH_3$	1	+0.064	–0.044	+0.030	–0.048
$S—CF_3$	1	+0.031	–0.064	+0.044	–0.077
F	1	–0.263	–0.138	+0.054	–0.401
»	4	–0.282	–0.114	+0.011	–0.355
Cl	1	+0.047	–0.045	+0.030	–0.051

* Methods of calculation: 1) INDO; 2*a*) MOX;[130] 2*b*) MOX;[129] 3) ASMO–SI;[130] 4) CNDO/2.[91]

(3) Nucleophilic attack by the fluoride anion takes place at positions 1 and 4 according to the highest positive charge in radical-cations of aromatic compounds containing donor substituents. The *ortho*-isomer is probably formed as a result of *ipso*-attack followed by oxidation and isomerisation of the arenonium ion[131]:

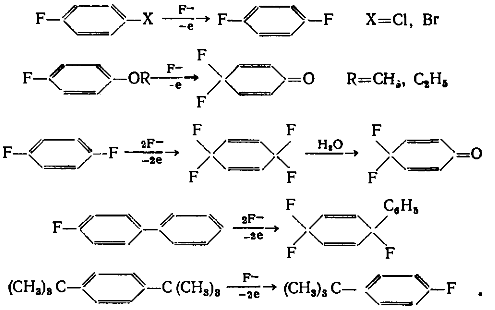


Direct confirmation of *ipso*-attack in anodic fluorination is provided by the substitution of chlorine, bromine, methoxyl, isopropyl, and t-butyl by fluorine to give fluorobenzene:



$X{=}Cl,\ Br,\ OCH_3,\ i\text{-}C_3H_7,\ t\text{-}C_4H_9$.

Furthermore, *ipso*-attack is clearly evident also in the anodic fluorination of *para*-disubstituted benzene derivatives[86,127,132]:



(4) Absence of direct *ortho*-attack is assumed because the positive charges at the *ortho*- and *meta*- positions are very similar in the radical-cations of toluene and t-butylbenzene, and in those of anisole and chlorobenzene the *meta*-charge even exceeds the charge in the *ortho*-position. Nevertheless, a considerable quantity of the *ortho*-isomer is formed in all these cases, whereas the *meta*-isomer has not been detected. Fluorobenzene provides an especially clear example, being the only case in which the *ortho*-isomer is not formed, although the general pattern of positive charge distribution in the radical-cation is qualitatively the same as with other donor substituents. This fact is readily explained in terms of *ipso*-attack (migration of fluorine is impossible in the corresponding arenonium ion):

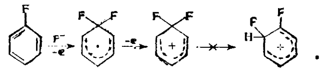
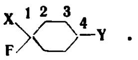


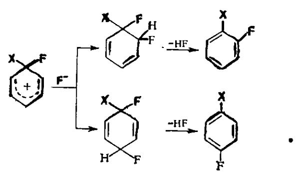
Table 6. Distribution of charge density in the cation



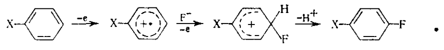
X	Y	Calcn.*	Charge density on atom			
			1	2	3	4
H	F	1	0.251	0.150	−0.072	0.508
H	F	2	0.186	0.135	−0.075	0.421
F	H	1	0.493	0.112	−0.026	0.300
F	H	2	0.399	0.120	−0.032	0.230
F	F	1	0.490	0.122	−0.057	0.527
F	F	2	0.399	0.118	−0.073	0.450
Cl	H	1	0.288	0.127	−0.012	0.244
CH$_3$	H	1	0.267	0.140	−0.026	0.248
F	*t*-C$_4$H$_9$	1	0.498	0.090	−0.021	0.267
F	O—CH$_3$	1	0.495	0.100	−0.045	0.414
F	C$_6$H$_5$	1	0.500	0.085	−0.009	0.252
F	*p*-C$_6$H$_4$F	1	0.481	0.091	−0.013	0.241

*Methods of calculation: 1) INDO; 2) CNDO/2.[91]

(5) *ipso*-Attack by the fluoride anion may result also in formation of the *para*-isomer:



A similar process may, perhaps, supplement the above *ECE* mechanism:



(6) The arenonium ion formed after *ipso*-attack can be stabilised only at *ortho*- and *para*-positions, as follows from the calculated positive charge distributions in these cations (Table 6).

(7) In conclusion it must again be emphasised that aromatic compounds containing donor substituents undergo anodic oxidation in the presence of the fluoride anion at potentials considerably lower than 2.87 V. Under these conditions oxidation of the fluoride anion to the radical is impossible, so that homolytic processes are excluded. For this reason we can speak of "pure" cases of the orientation of nucleophilic attack on aromatic radical-cations during anodic fluorination. The differences between orientation on anodic fluorination and on acetoxylation, cyanation, and methoxylation can evidently be regarded as contributions by the homolytic process in acetoxylation and cyanation.

2. Acceptor Substituents

Anodic processes involving aromatic compounds containing acceptor substituents (C_6H_5–A) have been very little studied: one paper was published in 1971, on the anodic fluorination of trifluoromethylbenzene[136], and in 1975 three communications appeared on anodic trifluoroacetoxylation[133–135]. The scarcity of publications in this field is due to the very high anodic potential (2.5–3.5 V) required for the oxidation of compounds of type C_6H_5–A. At such high potentials oxidation of the substrate is accompanied by many secondary processes—oxidation of the solvent, other components of the electrolyte, and, of course, the traces of water always present as impurity even in carefully dried aprotic solvents.

Introduction into an aromatic ring of an acceptor instead of a donor substituent leads to substantial changes in the proportions of products of anodic fluorination at platinum in acetonitrile. Knunyants et al. have shown that, when compounds containing such substituents as acetyl, methoxycarbonyl, fluoroformyl, cyano, and trichloromethyl are fluorinated[122], all three possible fluorinated isomers are formed in the relative proportions *ortho* > *meta* > *para* (Table 7). Unexpectedly, the pattern of distribution of fluorinated isomers from acetophenone, methyl benzoate, and benzonitrile was remarkably similar to the distribution obtained on the trifluoroacetoxylation of these compounds[134]. Exceptions were trifluoromethylbenzene (anodic fluorination yields exclusively the *meta*-isomer) and nitrobenzene (equal quantities of *ortho*- and *meta*-isomers formed).

Certain conclusions arise from an analysis of results for the anodic fluorination of aromatic compounds containing acceptor substituents and their comparison with the calculated distributions of positive charge and spin density in the radical-cations.

1. The orientation of substituents is not determined by the density distribution of positive charge in the radical-cation (Tables 8 and 9). In some cases (trifluoromethyl, nitro) the orientation of the substitution of hydrogen by fluorine is even opposite to the charge distribution. Yet the orientation of trifluoroacetoxylation correlates well[134] with the distribution of charge in the radical-cations of

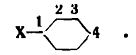
methyl benzoate, acetophenone, benzonitrile, trifluoromethylbenzene, and nitrobenzene. It was mentioned[134] that the calculations were made by the INDO method, but no specific results were given.

Table 7. Proportions of products in the substitutions $R.C_6H_5 \rightarrow R.C_6H_4.X$.

No.	R	Anodic reaction			Chemical reaction	X	Isomers, %			Ref.
		φ, V	anion	solvent*			o-	m-	p-	
1	$COOCH_3$	2.98	F·3HF	A		F	46	34	20	122
2	»	2.83	»	A		F	46	42	12	122
3	»	2.8	CF_3COO	T		CF_3COO	51	34	15	134
4	»	2.83	BF_4	M		»	69	—	31	135
5	»				$(C_6H_5COO)_2$	C_6H_5	58	17	25	121
6	COF	3.23	F·3HF	A		F	33	33	33	122
7	$CO-CH_3$	2.98	»	A		F	51	29	20	122
8	»	2.88	»	A		F	58	27	15	122
9	»	2.8	CF_3COO	T		CF_3COO	54	32	14	134
10	»	2.93	BF_4	M		»	100	—	—	135
11	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	50	33	17	119
12	CN	3.23	F·3HF	A		F	56	29	15	122
13	»	2.8	CF_3COO	T		CF_3COO	45	30	25	134
14	»				$(C_6H_5COO)_2$	C_6H_5	60	10	30	121
15	CCl_3	3.13	F·3HF	A		F	37	37	25	122
16	CF_3	3.4	»	A		F	—	100	—	136
17	»	2.8	CF_3COO	T		CF_3COO	35	47	18	134
18	»	3.5	»	T		»	72	—	28	133
19	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	47	51	2	119
20	»				F_2+CF_3COOH	F	25	61	14	120
21	»				XeF_2+HF	F	32	54	14	103
22	»				$(C_6H_5COO)_2$	C_6H_5	29	41	30	121
23	NO_2	3.73	F·3HF	A		F	50	50	—	122
24	»	4.53	CF_3COO	T		CF_3COO	37	47	16	133
25	»	2.8	»	T		»	22	59	19	134
26	»				XeF_2+HF	F	19	51	12	103
27	»				F_2+CF_3COOH	F	20	65	15	120
28	»				$(C_6H_5COO)_2$	C_6H_5	62	10	28	121

* Solvents: A = CH_3CN; M = $CH_2Cl_2 + CF_3COOH$; T = CF_3COOH.

Table 8. Distribution of total charge density in the radical-cation



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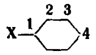
X	Calcn.*	Total charge on atom			
		1	2	3	4
$COCH_3$	1	−0.025	0.083	0.025	0.098
$COOCH_3$	1	0.033	0.076	0.034	0.094
COF	1	−0.049	0.096	0.027	0.106
CF_3	1	0.013	0.103	0.076	0.065
»	2	0.02	0.08	0.05	0.04
»	3	0.106	0.082	0.085	0.070
CN	1	0.138	0.068	0.055	0.098
NO_2	1	0.071	0.038	0.060	0.075
»	3	0.192	0.096	0.080	0.088

* Methods of calculation: 1) INDO; [122] 2) CNDO/2; [91] 3) MWH. [103]

2. The density of the unpaired electron is distributed very characteristically in aromatic radical-cations containing acceptor substituents (Table 10). The orbitals of the ring carbon atom have a very small spin density, with almost the whole density of the unpaired electron concentrated on substituent atoms. Furthermore, the difference in spin density between *o*-, *m*-, and *p*-carbon atoms is negligible, e.g. 0.001 and 0.009 in the radical-cations of acetophenone and nitrobenzene respectively. Such differences are quite unable to determine the orientation in substitutions.

Thus the rules of orientation in the substitution of hydrogen by fluorine in the anodic fluorination of aromatic compounds containing acceptor substituents are no longer unambiguously consistent with an *ECE* scheme (as occurs with donor substituents). It must be emphasised that the anodic fluorination of compounds of type C_6H_5-A has been conducted at potentials above 2.87 V, i.e. under conditions such that oxidation of the fluoride anion and hence radical fluorination are possible. However, a purely homolytic mechanism for these reactions would be an oversimplification. Indeed, the type of adsorption and the behaviour of organic compounds on platinum at such high potentials are completely uninvestigated. Yet the formation of surface oxides or higher fluorides produces a marked change in the adsorption and catalytic properties of the anode surface. The high energy of adsorption in these regions may prevent surface mobility of the oxidisable species, in particular of aromatic radical-cations.

Table 9. Distribution of π-component of charge in the radical-cation*



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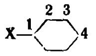
X	π-Component of charge on atom				X	π-Component of charge on atom			
	1	2	3	4		1	2	3	4
$COCH_3$	−0.114	0.073	0.009	0.119	CN	−0.012	−0.014	0.014	0.025
$COOCH_3$	−0.111	0.062	0.014	0.105	CF_3	−0.150	0.023	0.011	0.057
COF	−0.146	0.076	0.063	0.131	NO_2	−0.138	0.028	0.033	0.078

* Calculation by INDO method[122].

Table 10. Distribution of spin density in the radical-cation*.



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X	Spin density on atom				X	Spin density on atom			
	1	2	3	4		1	2	3	4
$COCH_3$	−0.067	0.008	−0.009	0.008	CF_3	−0.145	−0.065	−0.082	0.010
$COOCH_3$	−0.119	0.005	−0.012	0.004	CF_3**	0.141	0.072	0.076	0.002
COF	−0.078	0.005	−0.008	0.008	NO_2	−0.025	−0.010	0.003	−0.001

* Calculated by INDO method[122].
** Calculated by CNDO/2 method[91].

Therefore, as Mirkind has recently remarked[111], investigation of the mechanism of such reactions must first take into account the influence of heterogeneous factors on the rate and the direction of the electrode processes.

V. RADICAL-CATION PATH OF ELECTROCHEMICAL FLUORINATION IN HYDROGEN FLUORIDE

Right up to potentials of 2.8 V the oxidation of an aromatic compound at platinum in an aprotic medium involves the transfer of a single electron to the anode with formation of a radical-cation. It is therefore reasonable to suppose that the half-wave oxidation potential will be correlated with the energy of the highest occupied orbital and with the ionisation potential. Such a relation has been detected, and several workers have shown a linear correlation at platinum in acetonitrile with ionisation potentials[129,137–140] and with energies of highest occupied orbitals calculated by self-consistent field methods[141]. The linear dependence can be understood from a detailed examination of the energetic factors[139] governing the half-wave potential for the reaction Red → Ox + e:

$$E_{1/2}=\alpha IP+\Delta E_{\text{solvn.}}-\beta EA-\frac{T\cdot\Delta S^0}{\mathrm{F}}-\frac{RT}{F}\ln\frac{f_0D_R}{f_RD_0}+C,$$

where IP is the ionisation potential, α a coefficient representing the effect of adsorption on the electrode in the presence of the solvent, ΔE_{solvn} the difference in energy of solvation between Red and Ox, β a coefficient representing the effect of the adsorbed substance and the solvent on transfer of the electron, f an activity coefficient, F Faraday's constant, D the diffusion coefficient, EA the electron affinity of the metal (anode), and C a constant depending on the reference electrode.

When the same metal (platinum), solvent (acetonitrile), and supporting electrolyte are used, many terms in this equation will obviously be the same. When compounds of similar structure are oxidised, furthermore, the differences in ΔS^0 and activity coefficients may be expected to be small in comparison with the changes in ionisation potentials. The observed linear correlations can be represented by the equations

$$E_{1/2}=0.678IP-3.72^{138};$$
$$E_{1/2}=0.827IP-4.87^{139};$$
$$E_{\mathrm{p}/2}=0.75IP-4.55^{142}\ (E_{\mathrm{p}}-\text{peak potential})\ .$$

A correlation between ionisation potentials and oxidation half-wave potentials (at platinum in acetonitrile) has been observed not only with aromatic compounds but also with alkenes and alkanes[143].

However, this clear picture changes on passing to systems in other solvents (Table 11). Thus alkanes undergo anodic oxidation in acetonitrile at potentials above 3.9 V.[143] But on the addition of a strong acid, trifluoroacetic, the oxidation potential of these compounds drops sharply (by about 0.5 V), and corresponding oxidation peaks can be recorded by cyclic voltammetry[144]. Further considerable fall in oxidation potentials is observed in a strongly acid medium—fluorosulphuric acid—in the absence of acetonitrile[145]. An analogous pattern is evident with anhydrous hydrogen fluoride[147], in which the half-wave potentials are more than 1.0 V lower. It must be stressed that reversible processes, similar to those in acetonitrile, are observed in the oxidation of aromatic compounds at platinum both in fluorosulphuric and in hydrofluoric acids. Thus long-lived radical-cations are formed by the oxidation of perfluorinated aromatic compounds in fluorosulphuric acid[146]; the oxidation of perylene in hydrogen fluoride involves formation of a radical-cation at +0.12 V and irreversible transfer of a second electron with formation of a bication at +0.69 V.[147] Irreversible transfer of two electrons to the anode has been recorded in the oxidation of alkanes. Thus replacement of acetonitrile by fluorosulphuric or hydrofluoric acid results merely in a sharp quantitative fall in the oxidation potentials of organic compounds on platinum: the qualitative character of the oxidation processes themselves remains unchanged, since the same products are formed and the same dependence of half-wave potential on ionisation potential is maintained.

Quite different changes in electrochemical processes are evident on passing from organic solvents to water. For example, the rate of oxidation on platinum falls with increase in chain-length of the hydrocarbon and decrease in its ionisation potential[148]: i.e. an antiparallel dependence is observed. The reason is the completely different character of the process: considerable degradative chemisorption of the organic molecule occurs, accompanied by dehydrogenation and cracking[137,149,150].

Table 11. Oxidation potentials of organic compounds on platinum*.

Compound	$E_{1/2}$, B^{138,143} CH$_3$CN	$E_{\mathrm{p}/2}$, V^{145,146} HSO$_3$F	$E_{1/2}$, V^{147} HF	Compound	$E_{1/2}$, B^{138,143} CH$_3$CN	$E_{\mathrm{p}/2}$, V^{144} CH$_3$CN+CF$_3$COOH	$E_{\mathrm{p}/2}$, V^{145,146} HSO$_3$F
Naphthalene	1.77		0.65	Cyclohexene	2.58		
Mesitylene	2.03		0.91	But-2-ene	2.79		
p-Xylene	2.09		0.96	Pent-1-ene	3.27		
Toluene	2.21		1.17	But-1-ene	3.31		
Benzene	2.53		1.32	Propene	3.27		
Chlorobenzene	2.60		1.34	Ethylene	3.43		
Trifluorobenzene		1.07		Octane	>3.9	3.33	2.17
Pentafluorobenzene		1.13		Heptane	»	3.33	2.26
Hexafluorobenzene		1.32		Hexane	»	3.37	2.39
Perfluorobenzene		0.55		Pentane	»	3.41	2.54

* Potentials given relative to the normal hydrogen electrode.

Thus the anodic oxidation of aromatic compounds at platinum in hydrofluoric and chlorosulphuric acids and in aprotic organic solvents (acetonitrile) involves the transfer of one electron to the anode with formation of a radical-cation. In the absence of a nucleophile[82] the phenyl radical-cation rapidly eliminates a proton with subsequent recombination of radicals to give biphenyl or polyphenylenes:

$$C_6H_6\xrightarrow{-e}C_6H_6^{+\cdot}\xrightarrow{-H+}C_6H_5^{\cdot}\ .$$

Nyberg considers[151–154] that the mechanism of the formation of biphenyls consists in direct recombination of radical-cations with subsequent elimination of two protons[151]. In a later investigation of cross dimerisation he concluded[115] that the formation of dimeric products was the result of electrophilic attack on the radical-cation of the unoxidised aromatic molecule diffusing towards the electrode.

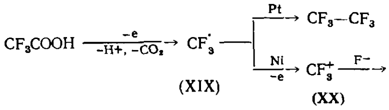
The anodic oxidation of benzene at platinum in hydrogen fluoride is very similar[158] to these processes: an electrically conducting polyphenylene film is formed, resembling soft graphite in its behaviour towards X-rays. The voltage in the cell does not exceed 1.1 V:

$$C_6H_6\xrightarrow[\text{HF}]{\text{Pt; 1.1 V}}(C_6H_{6-x})_n\ .$$

Polymer films of the same type have been obtained from naphthalene and toluene at low voltages[158]. The probable explanation of these results is that smooth platinum in hydrogen fluoride is an example of a "purified" electrode. Indeed, adsorption of the fluoride anion is probably the lowest for any anion at potentials up to 1.5 V.[155] Adsorption of fluoride ions on platinum begins only at higher potentials, which is explained by their entry into the oxide film[156]. Thus platinum at 1.0 V in hydrogen fluoride contains no adsorbed species, and under these conditions benzene and its homologues undergo the above "mild" oxidation. Comparison with oxidation results in acetonitrile[82,137–139] suggests that, in the limiting stage of the oxidation of aromatic compounds, charge is transferred to platinum through a layer of adsorbed acetonitrile molecules, which requires a considerable consumption of energy. A significant gain in energy ΔE_{solvn}, leading to a decrease in half-wave potential, is obtained also from the strong solvation of radical-cations in hydrogen fluoride.

Similar results have been obtained also at a nickel anode[158]. When benzene and toluene are oxidised at voltages up to 1.5 V in hydrogen fluoride, electrically conducting graphitic electrode coatings are formed, having the same elementary composition and structure as on a platinum anode. The yield of such "graphite" is quantitative. Polymerisation in attempts at the electrochemical fluorination of toluene had earlier been noted by Simons[2]. Similarly, an attempt at the electrochemical fluorination of anisole on nickel in hydrogen fluoride failed because of a rapid fall in conductivity and the separation of a black polymer[80]. Products of the polymerisation of benzene in this solvent were obtained also by Kokhanov[81].

Thus the products obtained at low potentials in hydrogen fluoride suggest that similar anodic processes occur on platinum and on nickel. As the anodic potential rises, however, considerable differences in behaviour appear between these anodes, owing to the different character of the adsorption of organic compounds on them. Electrolysis of a solution of hydrogen fluoride in trifluoroacetic acid at platinum, for example, yields mainly the Kolbe reaction product, hexafluoroethane, with a 2% yield of tetrafluoromethane[157] ($CF_4 : C_2F_6 = 2:100$), whereas at a nickel anode the latter is the main product (5 : 3). The probable reason for such a change in product composition is a difference in the energy of bonding of the adsorbed radical (XIX) with the anode surface, for on platinum this bonding is weak, the radical is mobile in the surface, and dimerisation occurs readily, whereas on nickel (more precisely on its difluoride) the adsorbed radical is firmly retained, dimerisation is difficult, and therefore oxidation to the cation (XX) is followed by the formation of carbon tetrafluoride:



$$CF_3COOH \xrightarrow[-H+,\ -CO_2]{-e} \underset{(XIX)}{CF_3^{\cdot}} \begin{cases} \xrightarrow{Pt} CF_3{-}CF_3 \\ \xrightarrow[-e]{Ni} \underset{(XX)}{CF_3^+} \xrightarrow{F^-} CF_4 \end{cases}$$

Still more significant differences are observed in the chemisorption of the methyl radical. Electrolysis of an acetic-acid solution of potassium fluoride at platinum yields ethane, as would be expected. At nickel the main product is tetrafluoromethane (44%) accompanied by fluoroform (7%), while the yield of the dimer of the methyl radical (ethane) is only 2%. In the Reviewer's opinion the formation of fluorinated products does not involve oxidation of the fluoride anion but consists in intermediate generation of organic radical-cations at the anode followed by "ionic fluorination". The organic radical-cation eliminates a proton with formation of a radical, which is rapidly oxidised to the cation and stabilised by addition of a fluoride anion. Thus the anodic fluorination of alkanes on nickel (just as on platinum) can be represented by an EC_bEC_N scheme:

$$CH_3COO^- \rightarrow CH_3COO^-\ (ads) \xrightarrow{-e} CH_3COO^{\cdot}\ (ads) \xrightarrow{-CO_2} CH_3^{\cdot}\ (ads) \xrightarrow{-e}$$
$$\rightarrow CH_3^+\ (ads) \xrightarrow{F^-} CH_3F\ (ads) \xrightarrow[(E)]{-e} CH_3F^{+\cdot}\ (ads) \xrightarrow[C_b]{-H+}$$
$$\rightarrow CH_2F^{\cdot}\ (ads) \xrightarrow[(E)]{-e} CH_2F^+\ (ads) \xrightarrow[(C_N)]{F^-}$$
$$\rightarrow CH_2F_2\ (ads) \xrightarrow[-H+]{-2e} CHF_2^+\ (ads) \xrightarrow{F^-} CHF_3\ (ads) \xrightarrow[-H+]{-2e} CF_3^+\ (ads) \xrightarrow{F^-} CF_4\ .$$

The energy of adsorption of alkanes on nickel (difluoride) is very large, and they are firmly retained on the anode. As fluorination proceeds, the bonding of alkanes to the surface becomes weaker, and polyfluoroalkanes can now be described from the anode. This difference in adsorption energy between alkanes and perfluoroalkanes is the reason for the predominant formation of only completely fluorinated compounds.

The present scheme has recently been confirmed[158] by a modified method of pulse polarography. Fluorination can be interrupted at any stage, depending on the duration of the anodic current pulse, with predominant formation of either methyl fluoride, difluoromethane, or fluoroform. This is explained by the possibility of desorption of incompletely fluorinated compounds when anodic polarisation of the electrode is switched off.

Pivalic acid behaves similarly to acetic acid. On oxidation at nickel in the presence of the fluoride anion the main product is perfluorobutane, with very little rupture of carbon–carbon bonds:

$$(CH_3)_3CCOOH \xrightarrow[-CO_2]{-e,\ -H+} (CH_3)_3C^{\cdot}\ (ads) \xrightarrow[-e,\ HF]{F^-,Ni} \underset{10}{C_4F_{10}} + \underset{:\ 1}{C_3F_8} + \underset{:\ 2}{C_2F_6} + \underset{:\ 1}{CF_4}\ .$$

Thus the fluorination of acetic and pivalic acids exemplifies the close analogy between these reactions and Simons electrochemical fluorination. Significantly, this analogy extends even to such "details" as the effect of the purity of the nickel anode and the material of the cathode on the yield of perfluorinated products[157, 158].

It is noteworthy that the formation of fluorinated products in the electrolysis of an acetic-acid solution of potassium fluoride at a nickel electrode is observed at a potential of 2.6 V, which corresponds to the only inflexion on the polarisation curve. This inflexion is undoubtedly due to oxidation of the acetate ion[157]. It has recently been shown[159] by a galvanostatic pulse method that on nickel the oxidation of acetic acid in anhydrous hydrogen fluoride precedes the start of oxidation of the fluoride anion. Other workers have found[160] that 2-chloroethanol is oxidised at a rotating nickel disc electrode in hydrofluoric acid also before the fluoride ion is oxidised.

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Thus the above account can be summarised by a general scheme of anodic fluorination of organic compounds in which the first step is adsorption of the organic molecule on the electrode and its oxidation to the corresponding radical-cation, whose subsequent fate is governed both by the structure of the initial organic compound and by the character of its adsorption on the electrode. When oxidised on platinum, the radical-cations of aromatic compounds and alkenes react directly with the fluoride anion present in the electrolyte; those of saturated compounds usually eliminate a proton. The organic radicals formed in both cases are rapidly oxidised on the anode to the corresponding cations, whose stabilisation is effected by elimination of a proton or addition of a fluoride anion. During oxidation on nickel the organic compounds and their radical-cations are firmly adsorbed on the electrode surface. Only polyfluorinated organic molecules can be desorbed from the surface of the nickel anode, which is the probable reason for the predominant formation of perfluorinated products.

The anodic fluorination of organic compounds does not usually involve oxidation of the fluoride anion to the radical (with subsequent homolytic reaction): carbon–fluorine bond formation results from ionic fluorination.

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Fluorinated Ketenimines

N.P.Gambaryan

Methods of obtaining imines of fluorinated ketens are surveyed, together with their dimerisation and nucleophilic addition. Cycloaddition at the carbon-nitrogen bond and 1,4-dipolar cycloaddition involving the aromatic ring are most characteristic of fluorine-containing *N*-arylketenimines. A two-stage mechanism is suggested, involving intermediate formation of small rings. The Review concludes with 92 references.

CONTENTS

I. INTRODUCTION

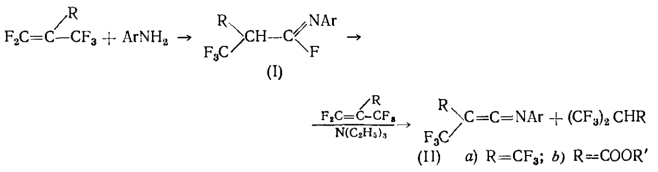
Imines of ketens were first obtained by Staudinger[1] in 1920, but their chemical properties have been studied only during recent years. Trialkylketenimines are unstable, so that the diaryl and mainly the triaryl derivatives have been investigated. Replacement of alkyl by trifluoromethyl groups greatly improves the stability both of ketens and of their imines, and hence imines of bistrifluoromethylketen provide a convenient model for studying the properties of aliphatic ketenimines.

Imines of ketens are of interest as dehydrating agents in peptide synthesis, as coreagents in oxidations with dimethyl sulphoxide, and especially as substrates in numerous cycloadditions with nucleophilic multiple bonds and dipolar compounds. The great variety of reactions involving cycloaddition is due to the fact that triarylketenimines react not only at the C=C and C=N bonds of the cumulative system but also at carbon or nitrogen with involvement of the aromatic rings, behaving in the latter reactions formally as dienes or nitrogen heterodienes. As a result, diverse carbocyclic and heterocyclic compounds are made available.

Reviews[2,3] have appeared during recent years, covering methods of preparation and reactions of ketenimines, but they contain hardly any information on fluorine-containing ketenimines. Nevertheless, fluoroketens and their imines exhibited a characteristic general feature of organofluorine compounds: the electron-accepting character of trifluoromethyl groups increases the electrophilic activity of bistrifluoromethylketen and its imines, which become capable of many reactions quite uncharacteristic of their unfluorinated analogues. Fluoroketens have been surveyed in Ref. 4. The present Review is concerned mainly with imines of bistrifluoromethylketen as the most readily available and thoroughly studied fluorinated ketenimines. Special attention is paid to *N*-aryl derivatives, since they reveal the effects of electron-donating and electron-accepting substituents on the activity of the cumulative bond system. Furthermore, the reactions of *N*-arylketenimines involving the aromatic ring are most interesting.

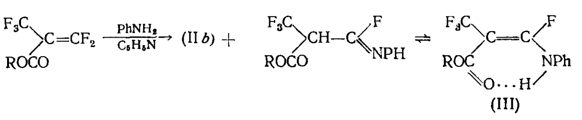
II. METHODS OF PREPARATION

A broad study of ketenimines became possible only after a simple general method of preparation was developed in 1973.[5,6] The latter was based on the reaction of perfluoroalkenes with primary amines, the result of which was determined by the ratio of the reactants. With perfluoroisobutene and perfluoromethacrylic esters excess of the amine gives difficultly separable mixtures of products. With excess of the alkene in the presence of catalytic quantities of triethylamine, on the other hand, excellent yields of the corresponding *N*-arylketenimines (II) are obtained in a single stage:



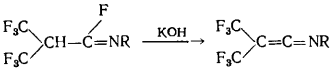
Thus a mixture of a fluoroalkene and triethylamine is a mild dehydrofluorinating agent, in which triethylamine acts as a carrier of hydrogen fluoride from the imidoyl fluoride (I) to the fluoroalkene. When pyridine is used instead of triethylamine, the reaction ceases at the stage of the imidoyl fluoride (I).

It is interesting that perfluoromethacrylic esters yield not only the imidoyl fluorides (I) but also the isomeric enamines (III):



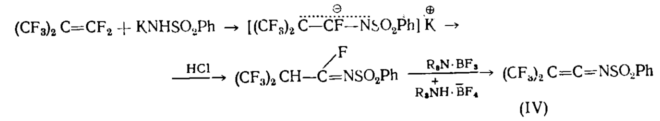
The comparative stability of the latter (III) is obviously due to the presence of an intramolecular hydrogen bond between the amino-group and the alkoxycarbonyl group. This is confirmed by the fact that the ratio of the latter to the former isomer increases with decrease in the ability of the solvent to form a hydrogen bond[6,7].

A second general method for preparing fluorinated ketenimines is the dehydrofluorination of imidoyl fluorides with powdered caustic potash in ether, which has been used to obtain the most diverse *N*-aryl-, *N*-alkyl-†, and *N*-cycloalkyl-ketenimines[5]‡:



(II *a*)

Such weak nucleophiles as benzenesulphonamide do not react with perfluoroisobutene. *N*-Benzenesulphonylbistrifluoromethylketenimine can be obtained as a stable adduct with potassium fluoride by treating perfluoroisobutene with the potassium salt of benzenesulphonamide; the free ketenimine (IV) is obtained by the action on the imidoyl fluoride of a mild dehydrofluorinating agent, such as the complex of triethylamine with boron trifluoride[9,10]:

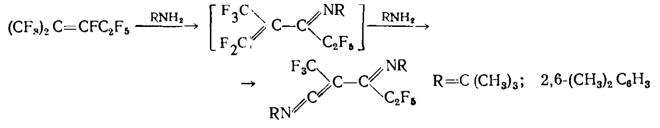


$$(CF_3)_2C{=}CF_2 + KNHSO_2Ph \rightarrow [(CF_3)_2\overset{\ominus}{C}{-}CF{-}NSO_2Ph]\overset{\oplus}{K} \rightarrow \xrightarrow{HCl} (CF_3)_2CH{-}CF{=}NSO_2Ph \xrightarrow[R_3\overset{+}{N}H\cdot\bar{B}F_4]{R_3N\cdot BF_3} (CF_3)_2C{=}C{=}NSO_2Ph$$

(IV)

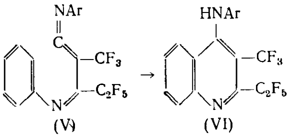
N-*p*-Nitrophenylbistrifluoromethylketenimine can be prepared similarly from the imidoyl fluoride only by means of this complex[11].

The reaction of fluoroalkenes with primary amines extends even to perfluoroisohexene[12]:



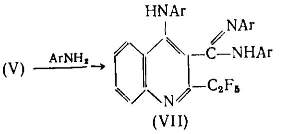
$R{=}C(CH_3)_3$; $2,6\text{-}(CH_3)_2C_6H_3$

N-Arylketenimines (V) in which an *ortho*-position is unsubstituted, especially when the ring contains electron-donor substituents, are cyclised under the reaction conditions to fluorinated quinolines (VI):



(V) (VI)

In the presence of a large excess of an aromatic amine the ketenimine (V) undergoes further reaction, ultimately with formation of the quinoline (VII)[13]:



(VII)

A less general method for preparing bistrifluoromethylketenimines is Staudinger's reaction[14]:

$$(CF_3)_2C{=}C{=}O + Ph_3P{=}NR \xrightarrow[-Ph_3PO]{} (CF_3)_2C{=}C{=}NR$$

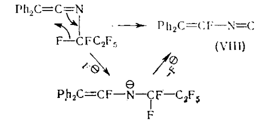
Bistrifluoromethylketen can be replaced by perfluoroisobutene, which reacts with tetraphenylphosphine imide, replacing two fluorine atoms by a phenylimino-group §[15]:

$$(CF_3)_2C{=}CF_2 + Ph_3P{=}NPh \xrightarrow[-Ph_3PF_2]{} (CF_3)_2C{=}C{=}NPh$$

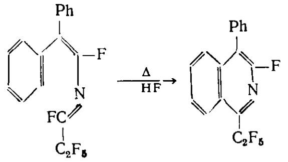
The Staudinger reaction can be used also to obtain ketenimines having an *N*-perfluoroalkyl group[18]:

$$(CF_3)_3CN{=}C{=}O + Ph_3P{=}CPh_2 \rightarrow (CF_3)_3CN{=}C{=}CPh_2$$

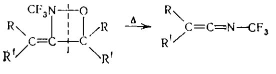
In contrast to perfluoro-t-butyl isocyanate, perfluoropropyl isocyanate, which contains mobile α-fluorine atoms, reacted with the yields to give the azabutadiene (VIII), obviously as a result of isomerisation of the intermediate ketenimine with migration of fluorine[18]:



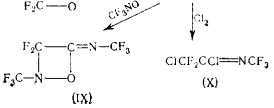
This rearrangement of a heterocumulene into a heterodiene can occur via a four-membered cyclic transition state or as a result of attack by a fluoride ion on the central carbon atom. An analogous isomerisation is found with bistrifluoromethylketen[19]. When heated, the azabutadiene (VIII) undergoes dehydrofluorination with ring closure, which provides a simple method for preparing a fluorinated isoquinoline[18]:



Ketenimines in which a trifluoromethyl group is attached to the nitrogen atom are formed also by pyrolysis of products of the cycloaddition of trifluoronitrosomethane to allenes[20]:



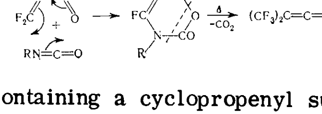
Ketenimines having fluorine atoms adjacent to the multiple bond, like the corresponding ketens, are unstable, and their formation in such a reaction can be judged from isolation of the cycloadduct (IX) or the chlorinated product (X)[21]:



Iminosulphuranes are analogous to iminophosphoranes in reacting with bistrifluoromethylthioketen to form *N*-alkyl- and *N*-phenyl-bistrifluoromethylketenimines[22]:

$$(CF_3)_2C{=}C{=}S \xrightarrow{RN{=}S{=}NR} (CF_3)_2C{=}C{=}NR$$

The remaining preparations of ketenimines having perfluoroalkyl groups attached to carbon are more specific in character. Thus *N*-alkylbistrifluoromethylketenimines are formed in the pyrolysis of a cycloaddition product of an isocyanate and perfluoromethacryloyl fluoride[23]:



Ketenimines containing a cyclopropenyl substituent are obtained by the interaction of perfluorobutyne with isonitriles in inert solvents; in the presence of an alcohol the

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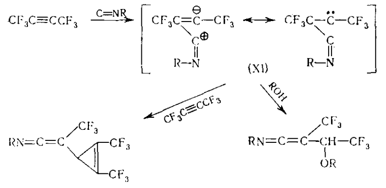
† Hexafluoroisobutyronitrile reacts with triethylamine to form a stable adduct[8], which can be regarded as a salt of the unsubstituted imine of bistrifluoromethylketen $(CF_3)_2C:C:NH.NH_3$.

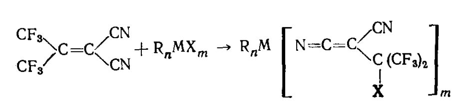
‡ The dehydrohalogenation of imidoyl halides is a general method for preparing unfluorinated ketenimines[2].

§ This reaction illustrates the analogy between the carbonyl and difluoromethylene groups[4,16,17].

intermediate equimolecular adduct (XI) reacts, not with another hexafluorobutyne molecule, but with the alcohol[24,25]:

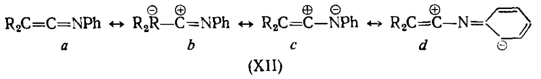


Finally, ketenimines containing *N*-organometallic groups are formed by the 1,4-addition of organo-silicon, -germanium, -tin, and -boron compounds to bistrifluoromethylmethylenemalononitrile[26,27]:



III. CHEMICAL PROPERTIES

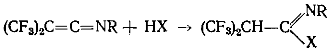
Ketenimines are iso-π-electronic with allenes and ketens, and can be represented by the resonance structures[28,29]



(XII)

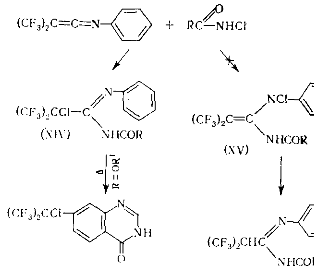
As the ketens, the electrophilic character of the central atom can be strengthened by attaching electron-donor substituents to the carbon atom. Furthermore, the structural features of ketenimines permit the reactivity of the heterocumulative bond system to be changed by attaching electron-donor or electron-acceptor substituents also to the nitrogen atom, the latter enhancing the electrophilic character. The most active electron acceptors exert in principle the same influence on the reactivity of ketenimines as does electrophilic catalysis, bringing their activity close to that for ketenimmonium salts[30]. Furthermore, the structure (XII*d*) indicates the possibility of reactions involving the aromatic ring of *N*-arylketenimines, in which the latter behave formally as 1,4-heterodienes— cf. (XXVII).

In conformity with the above, bistrifluoromethylketenimines react far more readily than unfluorinated ketenimines with water, alcohols, and amines to give the corresponding derivatives of hexafluoro-α-hydroisobutyric acid (XIII)[31]:



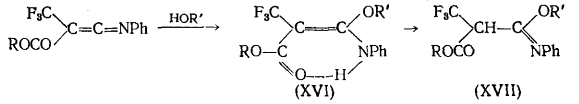
X=OH, OR, NR$_2$ (XIII)

This reaction does not answer the question—important for the chemistry of heterocumulenes—at which of the cumulative bonds the nucleophiles add on, since products of addition at the C=N bond, not stabilised by a hydrogen bond (Section II), would have immediately isomerised into the more stable end-products (XIII) ¶. However, the formation of the α-chlorohexafluoroisobutyramidines (XIV)[44] when the anil of bistrifluoromethylketen is treated with *N*-chloro amides indicates addition at the ethylenic bond in the ketenimine, since the product (XV) of addition at the C=N bond would have isomerised with migration of chlorine into the aromatic ring[33]:

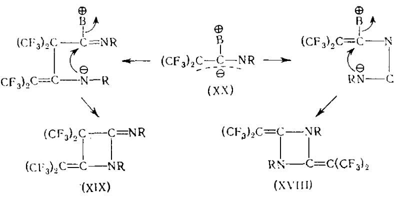


Cyclisation of the amidines (XIV) on being heated is a good method for the preparation of quinazolines.

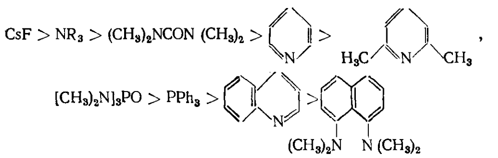
It is interesting that products formed by addition at the C=N bond in ketenimines — aminoacetals (XVI) — can be detected in the reactions of the anil of an alkyl trifluoro-β-*N*-phenyliminomethacrylate with alcohols; they rearrange comparatively slowly to imidic esters (XVII), a process which is irreversible[6], in contrast to the isomerisation of enamines into imidoyl fluorides (Section II):



In contrast to trialkylketenimines, *N*-alkyl- and especially *N*-aryl-bistrifluoromethylketenimines are stable, remaining unchanged even on prolonged heating †, However even such weak bases‡ as oxiran, dimethylformamide, benzylidenaniline, triethyl phosphate, pyridine, etc. cause rapid dimerisation of *N*-arylketenimines into symmetrical (XVIII) or unsymmetrical (XIX) dimers[11,31]:



Dimerising agents form the reactivity sequence



in which only the nitrogen heterocycles give rise to the symmetrical dimer (XVIII).[11] Comparison shows that the activity of a dimerising agent is determined mainly by its nucleophilicity, not its basicity. For example, such a strong base but weak nucleophile as naphthalene-1,8-bisdimethylamine[34] dimerises ketenimines more slowly than does the considerably less basic but more nucleophilic Hexametapol, triphenylphosphine, and tetramethylurea. Similarly,

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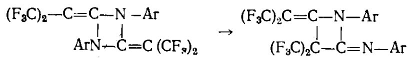
¶ Results on the addition of dialkyl phosphites at the C=N bond in the anil of bistrifluoromethylketen[32] are unreliable.

† *N*-t-Butylimines of fluorinated ketens on being heated decompose into isobutene and the corresponding nitrile[14].

‡ The poorer stability of unfluorinated ketenimines may be due to autocatalysis, since they themselves are quite strong bases. The basicity of imines of fluorinated ketens is depressed by the electron-accepting action of the trifluoromethyl groups.

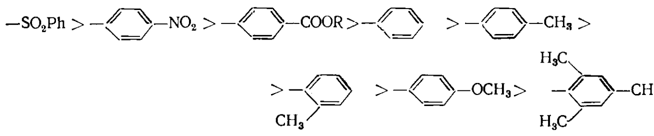
lutidine dimerises ketenimines more slowly than does pyridine[11]. The greater importance of the nucleophilicity of dimerising agents is consistent with the hypothesis that dimerisation begins with nucleophilic attack on the central carbon atom of the ketenimine to form the zwitterion (XX).

Unsymmetrical dimers are thermodynamically more stable than the symmetrical compounds, in accordance with which the latter rearrange into the former even under the influence of such weak bases as Hexametapol, tetramethylurea, pyridine, lutidine, and quinoline[11] §:



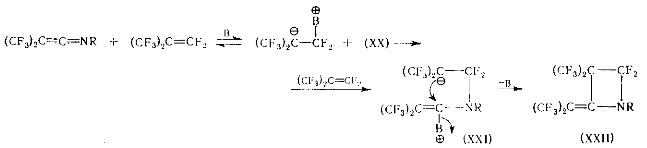
It is interesting that *para*-substituents in the aromatic ring have the same effect on the rate of rearrangement of symmetrical into unsymmetrical dimers as on the activity of the ketenimines.

The relative activities of fluorinated ketenimines have been studied in nucleophilic addition, dimerisation, and cycloaddition involving the aromatic ring. The anils of alkyl trifluoro-β-*N*-phenyliminomethacrylates are more active than the anil of bistrifluoromethylketen[6], since alkoxycarbonyl groups are stronger electron acceptors than is the trifluoromethyl group[37]. As already stated with regard to the effect of *N*-substituents, increasing the electron density on the nitrogen should diminish the electrophilic activity of the central carbon atom of the cumulative system. Indeed, the activities of *N*-substituted bistrifluoromethylketenimines are antiparallel to the basicities of the nitrogen in them[11]:



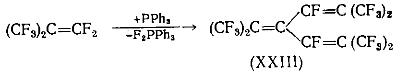
where the *N*-benzenesulphonyl derivative is the most active, and the *N*-alkyl compounds are the least active. The activity of imines of fluorinated ketens depends not only on the basicity of the nitrogen atom but also on the bulk of the reactant and of the substituent, especially in cycloadditions. Thus *N*-phenylbistrifluoromethylketenimine adds methanol and ethanol in 1–2 h, whereas with t-butyl alcohol the reaction is not complete after 6 months[44]; *N*-mesitylbistrifluoromethylketenimine adds alcohol considerably more slowly than does *N*-phenylketenimine, and is dimerised with immeasurably greater difficulty than any other ketenimine[11]; and *N*-*o*-tolybistrifluoromethylketenimine dimerises more slowly than does the *para*-isomer.

It is interesting that the presence of perfluoroisobutene slows down by more than 99% the dimerisation of imines of fluorinated ketens under the influence of tertiary amines. Perfluoroisobutene not only tends to inhibit dimerisation but also recaptures the mesomeric anion (XX); the resulting carbanion (XXI) undergoes cyclisation to the azetidine (XXII) with regeneration of the tertiary amine. Thus the extremely electrophilic character of perfluoroisobutene enables it to compete successfully with ketenimines both in bonding the amine and in recapturing the betaine (XX). Dimerisation is suppressed, and the main reaction product is the corresponding azetidine (XXII)[38]:



The same result is obtained in the presence of alkali-metal fluorides. Such mixed dimerisation of ketenimines with perfluoroisobutene provides an excellent method for preparing fluorinated azetidines.

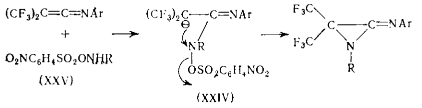
Triphenylphosphine is more active than tertiary amines in catalysing the dimerisation of activated alkenes and the Michael reaction[39,40]. However, it cannot be used to catalyse the cycloaddition of perfluoroisobutene to ketenimines: perfluoroisobutene reacts not only in preference to the ketenimine but also irreversibly, being converted ultimately into the conjugated triene (XXIII) ¶:



$$(CF_3)_2C{=}CF_2 \xrightarrow[-F_2PPh_3]{+PPh_3} (CF_3)_2C{=}C(CF{=}C(CF_3)_2)_2$$

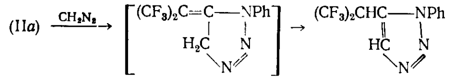
(XXIII)

In the synthesis of azetidines the carbanion (XXI) is stabilised by intramolecular nucleophilic substitution of the group B with closure of the four-membered ring. Nucleophilic elimination of imines of fluorinated ketens is accomplished similarly but at the ethylenic bond of the ketenimine. The carbanion (XXIV) is then obtained by the action of substituted amides (XXV) on the fluorinated ketenimines.

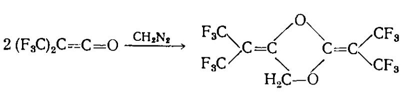


It is interesting that the direction of the reaction is predetermined by the nature of the leaving group: whereas chlorine migrates to the anionic centre of the molecule—cf. (XV)—the sulphonyloxy-group is readily detached with closure of the three-membered ring.

Nucleophilic elimination and formation of the unsymmetrical dimer (XIX) are among the few examples of cycloaddition at the ethylenic bond in imines of fluorinated ketens. Almost all cycloadditions involving unfluorinated ketenimines, on the other hand, take place at the ethylenic bond in the heterocumulene[2] †. An exception is the reaction of triarylketenimines with diazomethane[43]. Imines of fluorinated ketens also react with diazomethane at their C=N bond[44].



Bistrifluoromethylketen gives with diazomethane a cyclic trimer as a result of the reaction of both keten molecules at the carbonyl group[45]:



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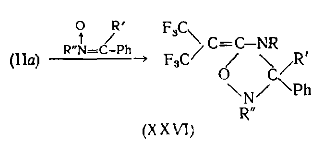
§ Symmetrical dimers of ketens (cyclobutanediones) isomerise into the unsymmetrical dimers in the presence of aluminium chloride; the reverse rearrangement takes place in the presence of bases[35]. Symmetrical dimers of unfluorinated ketenimines have not been described; for the only examples of unsymmetrical dimers see Ref. 36.

¶ Perfluorocyclobutene and butadiene give a 1 : 1 adduct with triphenylphosphine[41,42].

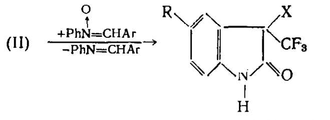
† Since hardly any information is available on aliphatic ketenimines[2], imines of bistrifluoromethylketen must be compared with those of aromatic ketens.

With nitrones unfluorinated ketenimines give products resulting from addition at the ethylenic bonds[46]. Imines of fluorinated ketens, on the other hand, form with triphenyl and *N*-methyl-*α*-phenyl nitrones cyclic adducts at the C=N bond — oxa-2,4-diazolidines (XXVI)[47]:

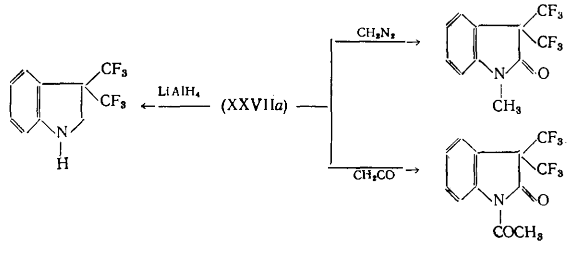


(XXVI)

In the cycloadditions discussed hitherto the fluorinated ketenimines have behaved as 1,2-dipolar compounds. As already mentioned — cf. (XII) and (XV) — however, with *N*-arylketenimines reactions involving the aromatic ring are also possible, in which these derivatives behave formally as 1,4-dipolar compounds. An example of this type is the unusual reaction undergone by imines of fluorinated ketens with *α*-aryl *N*-phenyl nitrones, in which fluorinated oxindoles (XXVII) have already formed on cooling[48], instead of cycloaddition products:

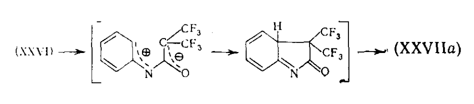


(XXVII) *a*) $X=CF_3$ *b*) $X=CO_2R'$



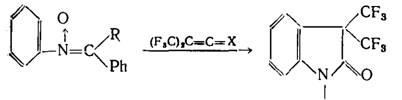
The structure of (XXVII*a*) is confirmed by cross synthesis, as well as by its chemical reactions. The oxindole (XXVII*a*) is formed also from oxadiazolidines (XXVI: R = C_6H_5). On standing for a long time or on being heated in a solvent, the latter compounds break down into the oxindole (XXVII*a*) and the corresponding Schiff bases. Isolation of products of the 1,3-cycloaddition of triphenyl and *N*-methyl *α*-phenyl nitrones to *N*-arylbistrifluoromethylketenimines and their conversion into the oxindole (XXVII*a*) suggest that reaction with the latter nitrones may involve the formation of unstable oxadiazolidines, which decompose so easily into an oxindole and an imine that they cannot be detected even by spectroscopic methods.

Thus nitrones are ultimately donors of oxygen in their reactions with *N*-arylbistrifluoromethylketenimines, which is unusual for nitrones. The mechanism of this peculiar reaction of oxygen transfer can be represented[47]:



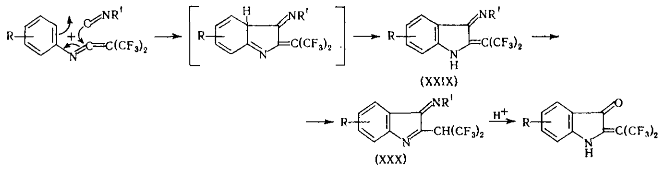
The betaine is stabilised by cyclisation at an *ortho*-position in the aromatic ring.

Substituted oxindoles (XXVII) are formed eventually also by the reaction of *N*-benzenesulphonylbistrifluoromethylketenimine and bistrifluoromethylketen[47] with *N*-phenyl nitrones, which, in contrast to the above reactions, involves the phenyl group of the nitrone:

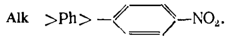


(XXVIII) X=O, NSO_2Ph; Y=$OCOCH(CF_3)_2$, $NHSO_2Ph$

Indole derivatives are obtained also by reaction between *N*-arylbistrifluoromethylketenimines and isocyanides[49]. The indogenimines (XXIX) formed by 1,4-dipolar addition under very mild conditions then isomerise into iminoindolenines (XXX), whose hydrolysis involves migration of hydrogen back to the nitrogen[49]:

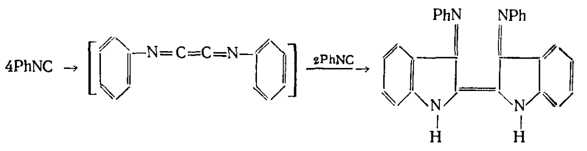


Reactions with isocyanides, similarly to nucleophilic addition and cyclodimerisation, are accelerated by electron-acceptor substituents in the aromatic ring of bistrifluoromethylketenimines, but restrained by electron-donor substituents. Whether in the imino-group or in the benzene ring, substituents have the opposite effect on the rate of isomerisation of indogenides into indolenines: indogenimines obtained from methoxyketenimine and alkyl isocyanides are the least stable. The reactivities of isocyanides with *N*-arylbistrifluoromethylketenimines fall in the sequence[50]



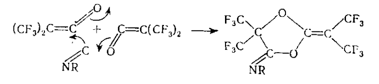
It is interesting that the reactivity sequence of isocyanides with nucleophilic acetylenic bonds is just the reverse[51]. This clearly indicates a difference in reaction mechanisms: whereas isocyanides react as nucleophiles with extremely electrophilic organofluorine compounds‡, they react as electrophiles with nucleophilic alkynes.

Unfluorinated triarylketenimines react with isocyanides only on irradiation, when heated, or in the presence of a catalyst. The reaction may involve the aromatic ring, the nitrogen atom, or a carbon atom, its direction being governed by the substituents in the aryl rings[53,54]. Only the tetramerisation of phenyl isocyanide



is accomplished at room temperature and without external assistance[49,54,55].

Bistrifluoromethylketen gives with isocyanides, as with diazomethane, a cyclic trimer in which both keten molecules have reacted at the carbonyl group[45], whereas unfluorinated ketens react at the ethylenic bond[52]:



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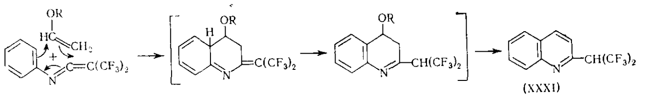
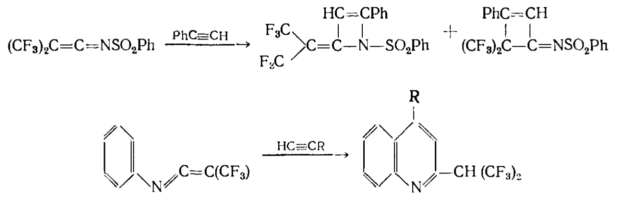
‡ The nucleophilicity of the carbene carbon atom is less in aryl than in alkyl isocyanides[52], and decreases on the introduction of electron-accepting substituents into the aromatic ring.

Ordinary alkenes are insufficiently nucleophilic and do not react with imines of fluorinated ketens. With especially nucleophilic vinyl ethers, however, *N*-arylbistrifluoromethylketenimines react even at room temperature, yet again by 1,4-cycloaddition with the ultimate formation of a fluorinated quinoline (XXXI)[56]:



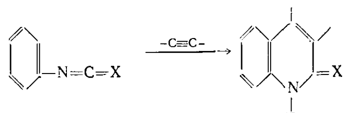
(XXXI)

Imines of fluorinated ketens react similarly with ethoxy- and phenyl-acetylenes (only the especially active *N*-*p*-nitrophenyl- and *N*-benzenesulphonyl-ketenimines react with the latter without heating). *N*-Benzenesulphonylbistrifluoromethylketenimine, which does not contain a conjugated bond system, gives a mixture of cyclic adducts formed at the C=N and C=C bonds, whereas *N*-arylketenimines react as nitrogen heterodienes with involvement of the aromatic ring[31,56]:



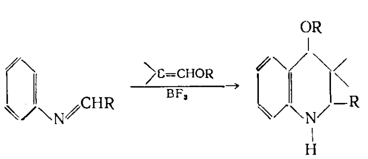
Various reactions of *N*-arylbistrifluoromethylketenimines involving the aromatic ring can be accomplished with good yields, usually with cooling or at room temperature, and provide a convenient method for preparing fluorinated heterocycles. The Reviewer considers reactions of this type most interesting, and will therefore discuss them in somewhat greater detail.

Apart from the processes discussed above, several other reactions have been discovered during recent years, usually achieved also under mild conditions, in which the cumulative or the azomethine bond with an attached aromatic ring behaves as a nitrogen heterodiene. Examples are the reactions of phenyl isocyanate[57–59] and of *N*-arylketenimines[60,61] with nucleophilic alkynes:

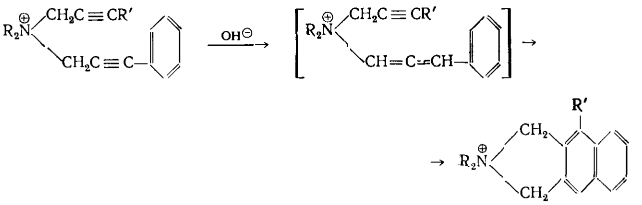


$X = O, CPh_2$

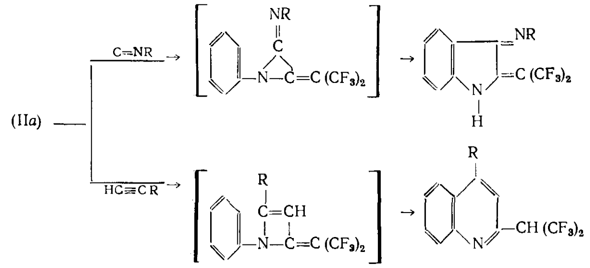
Formation of a quinoline ring by the reaction of vinyl ethers § with Schiff bases (in the presence of boron trifluoride)[62–64]

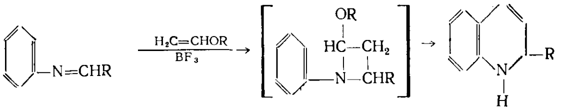


or with ammonium salts[65,66] has been widely studied. An ethylenic bond to which an aromatic ring is attached can also react as a diene under mild conditions[67,68]. Examples are the reaction of styrene with perfluorothioacetone[69] and the intramolecular cyclisation of amines and ammonium salts containing an *N*-arylprop-2-ynyl group[70,71]:



All these reactions are structurally similar to Diels–Alder reactions. Their mechanism has not been established, yet they have usually been regarded, in view of the isolation of final products to be expected from a mechanism of diene synthesis, as fresh examples of the Diels–Alder reaction¶. This approach seems unsound. Indeed, it is improbable that, under such mild conditions, an aromatic ring would react as a double bond of a diene. Typical Diels–Alder reactions represent concerted ($\pi 4_s + \pi 2_s$) addition, requiring very specific orientation of the reactants. They are therefore characterised by high negative entropies of activation: the pre-exponential factors in the rate constants are smaller by factors of 10^5–10^6 than would follow from collision theory[73,74]. Compensation for these rigorous demands on mutual reactant orientation is usually provided by a favourable energy balance in the reaction, with the disappearance of two double bonds and the formation of two σ-bonds. Such compensation is absent from reactions involving an aromatic ring, since they entail loss of the aromatic stabilisation energy. Yet they are usually accomplished under far milder conditions than are typical Diels–Alder reactions, which casts still greater doubt on the identification of these two types of processes. A two-stage rather than a synchronous mechanism is more probable for such reactions, involving intermediate formation of small rings subsequently stabilised by reaction with the aromatic ring†: e.g.





The best proof of a two-stage mechanism for reactions involving the aromatic ring would be isolation of compounds containing small rings and their conversion into the final heterocycles. However, this is not the simplest of tasks,

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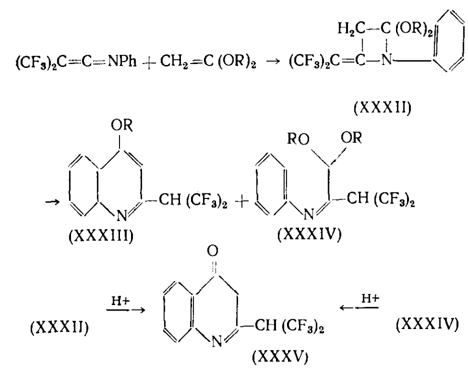
§ Isocyanides also react like alkenes with Schiff bases[72].

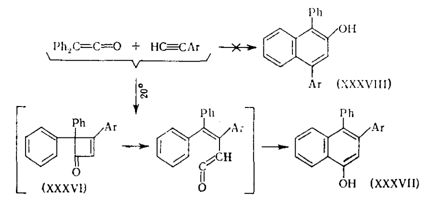
¶ An alternative mechanism with intermediate formation of cyclobutanone followed by isomerisation to a six-membered ring has been discussed[75].

† Such changes are well known with three-membered[76–79] and four-membered[80–85] rings.

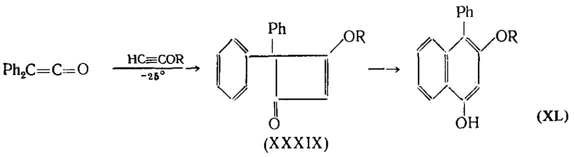
since small rings are very reactive[86,87]. Indeed, few data are available on the isolation of small rings in reactions of this type. Despite numerous attempts in the case of imines of fluorinated ketens, for example, only in a reaction with a keten acetal could a fairly stable product of cycloaddition at the C=N bond — the azetidine (XXXII) — be isolated. On prolonged storage at room temperature this azetidine is converted into the ethoxyquinoline (XXXIII) and the linear anil (XXXIV). Concentrated sulphuric acid converts both (XXXII) and its linear isomer into hexafluoroisopropyl-4-quinolone (XXXV)[56]:



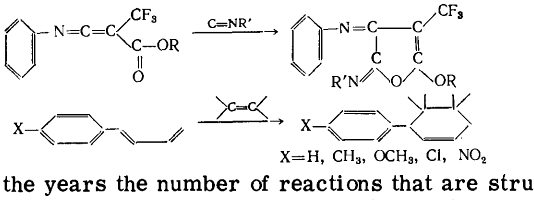
In the reaction of diphenylketen with arylacetylenes the intermediate product—cyclobutene (XXXVI)—could not be isolated, but the final formation of the 1-naphthol (XXXVII) instead of the 2-naphthol (XXXVIII) provided a forcible argument in support of a two-stage process[88]:



With the more reactive ethoxyacetylene, indeed, the cyclobutenone (XXXIX) could be isolated and converted into the 1-naphthol (XL)[84]:



Indirect support for a two-stage mechanism of "diene synthesis" involving an aromatic ring is that, when another conjugated multiple bond is present as well as the ring, this bond, of course, reacts[50,68,89]: e.g.



Over the years the number of reactions that are structurally similar to Diels–Alder reactions has so increased and their variety is so great that it would be naive to suppose that they all have the same mechanism. Both concerted and two-stage mechanisms have many variations. Formation of the two bonds may not be altogether simultaneous in a concerted mechanism[73,90]. Initial formation of charge-transfer molecular complexes is possible[91,92]. The first stage of two-stage reactions may produce betaines, perhaps in equilibrium with small rings. However, a covalent structure is more probable for the intermediate products, since substituents of the first and second kinds in the aromatic ring would have had a far greater effect in the case of betaines than is observed[73] ‡.

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Thus both in nucleophilic addition and in cycloaddition not only are imines of fluorinated ketens more reactive than unfluorinated ketenimines but they also undergo reactions that are unknown with the latter compounds. Another distinguishing feature of the fluorinated imines is that most cycloadditions involve the methine bond, not the ethylenic bond as with the unfluorinated analogues (perhaps because of steric factors, which are especially important in cycloaddition). Because the methine bond is less polar than the carbonyl bond, imines of bistrifluoromethylketen are less reactive than bistrifluoromethylketen itself. Reactions involving the aromatic ring, which are structurally similar to the Diels–Alder reaction but obviously occur by a completely different mechanism, extend significantly the synthetic possibilities of ketenimines.

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‡ For example, the rate of reaction of *N*-arylbistrifluoromethylketenimines with isocyanides decreases by factors of only 3–5 when an alkoxycarbonyl group is replaced by methyl.

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Four- and Five-membered Cyclic Disulphides

T.P.Vasil'eva, M.G.Lin'kova, and O.V.Kil'disheva

The principal methods for synthesising 1,2-dithiolans are surveyed, together with their advantages and disadvantages. Information is given on the geometry of the 1,2-dithiolan ring. The polarography, photolysis, and spectra of 1,2-dithiolans are discussed, and results are given for their polymerisation, reduction, oxidation, and chlorolysis, as well as the removal of a sulphur atom. Data are presented on the biological importance and application of 1,2-dithiolans. The major part of the review is devoted to the chemistry of unsaturated five-membered cyclic disulphides—the 3-thiones, 3-ones, 3-imines, and 3-ylidenes of 1,2-dithiolens—with methods of preparation and both chemical and physical properties. A detailed examination is made of their reactions with electrophilic and nucleophilic reagents, as well as condensations. Fields of practical application of 1,2-dithiolens are surveyed. The review concludes with 233 references.

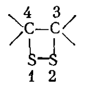
CONTENTS

I. INTRODUCTION

The chemistry of saturated and unsaturated four- and five-membered cyclic disulphides forms a new field, widely developed during the past decade. Saturated and unsaturated five-membered disulphides (1,2-dithiolans and 1,2-dithiolens) are present as fragments in certain antibiotics (gliotoxin, thiolutin, holomycin) and naturally occurring physiologically active compounds (α-lipoic and asparagusic acids, nereistoxin, brugine, etc.). Certain compounds find application as insecticides, antioxidants, and colorants.

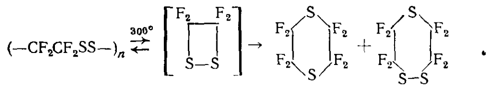
II. 1,2-DITHIETANS AND 1,2-DITHIETENS

Four-membered cyclic disulphides, 1,2-dithietans (I)



(I)

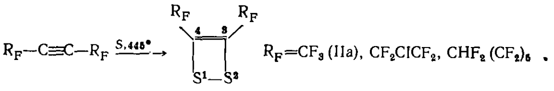
have not yet been obtained. It is known only that, when the pressure is lowered in the pyrolysis of polymeric perfluoroethylene disulphide, dithian and trithiepan are obtained. The mass spectra suggest the intermediate formation of tetrafluoro-1,2-dithietan (Ia), which at low temperatures is reconverted into the initial polymer[1]:



(Ia)

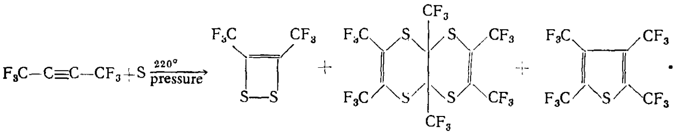
The instability of the almost planar 1,2-dithietan ring (I) is attributed to strong repulsion of the *p*,π electrons of the neighbouring sulphur atoms[1]. However, unsaturated four-membered cyclic disulphides, 1,2-dithietens (II), are more stable than the saturated analogues (I) because of the presence in the ring of an "aromatic" sextet of electrons[2].

Perfluorinated 1,2-dithietens (II) were first obtained by Krespan[3] by the action of sulphur on polyfluorinated alkynes[3,4]:



(II)

A yield of 80% of bistrifluoromethyl-1,2-dithieten (IIa) was prepared in this way[3]. At lower temperatures the yield does not exceed 26% owing to the formation of secondary condensation products[4]:

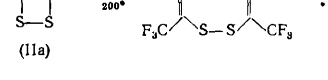


(IIa) 26% 29% 11%

However, 1,2-dithietens (II) cannot be obtained from acetylene and dimethyl acetylenedicarboxylate[4]. The first report that benzo-1,2-dithieten had been obtained[5] has proved to be erroneous[4].

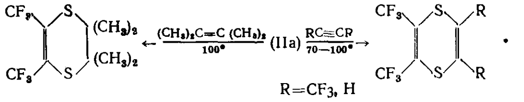
The 1,2-dithieten ring exhibits characteristic ultraviolet absorption in two ranges—at 231–243 and 334–340 nm[4].

The chemical properties of 1,2-dithietens are determined by the labile disulphide bond. Thus (IIa) dimerises slowly at 25°C, rapidly in the presence of weakly basic catalysts (triethylamine, ethanol); (IIa) is reformed when the dimer is heated to 200°C: [3,4]

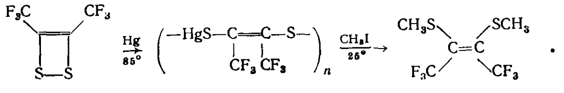


(IIa)

Cycloaddition at the disulphide bond occurs readily with alkenes and alkynes[3,4,6]:

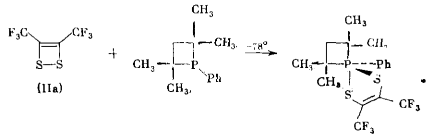


The presence of electron-donor substituents in the unsaturated hydrocarbons facilitates cycloaddition[6]. The action of mercury converts (IIa) into a polymer, which with iodomethane forms 2,3-bismethylthioperfluorobut-2-ene[6]:

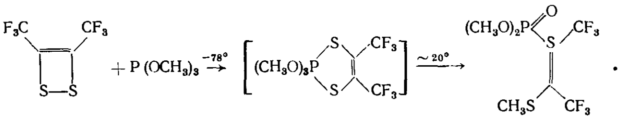


(IIa)

With phosphines and phosphites (IIa) yields sulphur-containing phosphorans[7]:



Methyl *o*-phenylene hydrogen, ethyl methyl hydrogen, and trimethyl phosphites react similarly. In the latter two cases the adducts are unstable, and undergo the Arbuzov rearrangement even at 20°C:[7]

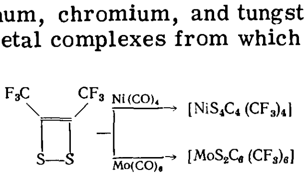


(IIa)

With transition-metal carbonyls (IIa) form complexes also with cleavage of the cyclic disulphide bond. Thus it gives a trimeric complex with octacarbonyldicobalt[8]:

$$Co_2(CO)_8 + (IIa) \rightarrow [(CF_3)_2C_2S_2Co(CO)]_3 \ .$$

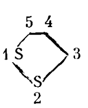
Nickel, molybdenum, chromium, and tungsten carbonyls form with (IIa) metal complexes from which the carbonyl group is absent[9]:



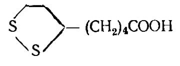
(IIa)

III. 1,2-DITHIOLANS

This survey of the literature on 1,2-dithiolans (III) mainly covers the period after 1963, for earlier investigations were summarised in a monograph[10]. Because of the great biological importance of α-lipoic (thioctic) acid (IIIa)



(III)



(IIIa)

results for this compound have been segregated as an independent topic[10], and will not be considered in detail here.

1. Methods of Preparation

(*a*) Oxidation of 1,3-dithiols

The most general method for obtaining 1,2-dithiolans is the intramolecular oxidation of 1,3-dithiols (Table 1).[10–23] Thus a substituted 1,2-dithiolan was first obtained by Reissert in 1906, by oxidising the dianilide of dithiomalonic acid[10]:

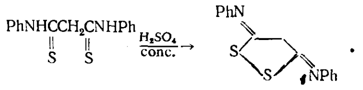
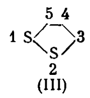


Table 1. 1,2-Dithiolans obtained by the oxidation of 1,3-dithiols.

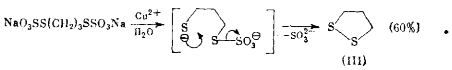
1,2-Dithiolan	Oxidant (temp., °C)	Yield, %	Ref.
 (III)	H_2O_2—KI (25°)	35*	12
	H_2O_2—KI (75°)	70*	12
	H_2O_2—KI (115°)	0	12
	I_2—$FeCl_3$	26*	12
	Pb $(OAc)_4$ (80°)	36*	12
	Pb $(OAc)_4$ (25°)	21—40*	12
	I_2—Et_3N	56*	13
3-$(CH_3)_2$**	*t*-BuOOH, Fe^{3+}	50	10
4-N $(CH_3)_2$	air	—	14
3-COOH	O_2, Fe^{3+}	66	10
	air, $FeCl_3$	74***	15
	H_2O_2, Fe^{3+}	15	10
4-COOH	H_2O_2	17	16
	H_2O_2—KI (75°)	57	16
	I_2—Et_3N	40	16
	$K_3Fe(CN)_6$	32	16
4-CH_2OH	H_2O_2 (75°)	70	16
4-$(CH_2OH)_2$	I_2	—	10
4-C_6H_5	I_2—Et_3N	73	13
4-SO_3H	I_2—H_2O	—	10
1,2-Dithiolan	Oxidant	Yield, %	Ref.
4-(=O)	I_2—Et_3N	—	13
	I_2	—	10
3,5-$(=O)_2$-4-$(CH_3)_2$		57	17
3,5-$(=O)_2$-4-$(C_2H_5)_2$	I_2, pyridine	80	17
3,5-$(=O)_2$-4-$(CH_2)_3$		82	17
3-(=O)-4-NHCOPh-5-$(CH_3)_2$	$FeCl_3$	50	10
3-CH_2COOH	O_2, Fe^{3+}	10	10
3-CH_2COOH-4-(=O)	I_2	24	18, 19
4-$(CH_2)_2COOH$	O_2—$FeCl_3$	1	20
4-$(CH_2)_3$ COOH	O_2—$FeCl_3$	42	20
3,5-$(COOH)_2$	I_2	65	21
	O_2, Fe^{3+}	77	10
4-$(NH_2 \cdot HCl)$	I_2—KI	60	22
3-$[(CH_2)_4COOH]$-4-(=O)	I_2	59	18
	I_2—KI	30	23
3-$[(CH_2)_4CO_2CH_3]$-4-OH	I_2—KI	75	23
4-CO $(CH_2)_3CO_2R$	I_2—KI	10	23

*Yield determined from concentration in solution (by ultraviolet spectrometry).

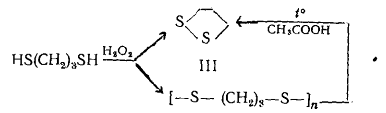
**Here and below the numeral indicates the position of the substituent in the ring (III).

***Yield of crude product.

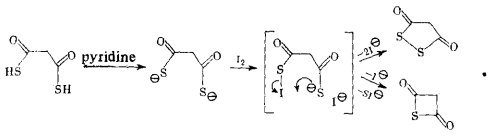
The early attempts at synthesising unsubstituted (III) usually yielded solid polymers or dimers, and only in 1950 did Affleck obtain (III)—in benzene solution—by the action of copper(II) chloride on trimethylene bisthiosulphate[11]:



A disadvantage of this method is secondary intermolecular oxidation to poly-1,2-dithiolans; on prolonged heating in acetic acid these are converted into (III):[12]

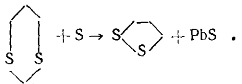


Intermediate formation of a monosulphenyl iodide is postulated in the oxidation of 1,3-dithiols (or 1,3-bisthiolic acids) to 1,2-dithiolans: e.g.[17]



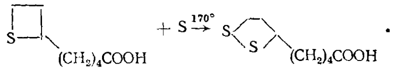
The intermediate undergoes either conversion into the cyclic disulphide or, with elimination of an SI⁻ ion, cyclisation to a four-membered sulphide[17].

High yields of various derivatives of 1,2-dithiolan (III) are obtained by the action of sulphur on the corresponding lead dithiolates[24]:



(III)

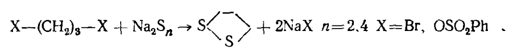
It is noteworthy that α-lipoic acid (IIIa) and its methyl ester can be prepared by introducing a second sulphur atom into the corresponding thietan derivatives[25]:



(III a)

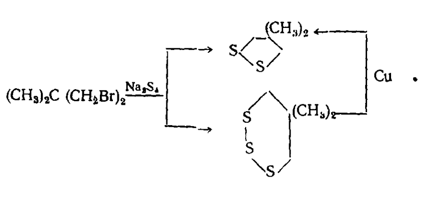
(*b*) Condensation of 1,3-dihalogeno-derivatives with alkali-metal polysulphides

The lower yields are responsible for the less frequent use made of the cyclisation of 1,3-dihalides (or bisarenesulphonic esters of 1,3-glycols) by means of alkali-metal polysulphides (Table 2):[26-28]



(III)

Higher yields of (III) are obtained with Na_2S_4 than with Na_2S_2. Use of the latter yields thietans as byproducts[10], whereas Na_2S_4 gives cyclic trisulphides, which are converted into disulphides (III) by boiling with copper powder[27]:



(*c*) Intramolecular cyclisation of β-mercaptothio-carboxylic acids

The most general method for obtaining 1,2-dithiolan-3-ones is intramolecular acylation of β-thiothiols (or their acetyl derivatives) containing an activated carboxyl:

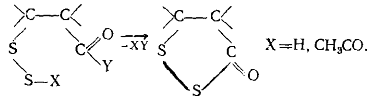
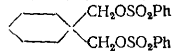


Table 2.

1,2-Dithiolan (III)	Initial compound	Reagent	Yield, %	Ref.
Unsubstituted	$Br(CH_2)_3Br$	Na_2S_2	9	
4-$(CH_3)_2$	$(CH_3)_2C(CH_2Br)_2$	K_2S_2	55	10
3,5-$(COOH)_2$	$CH_2[CH(Br)COONa]_2$	Na_2S_2	22	
Ditto	$CH_2[CH(Br)COOH]_2$	Na_2S_2	11	26
4-$(CH_2)_5$		Na_2S_4	47	27
4-$(CH_2OH)_2$	$(HOCH_2)_2C(CH_2Br)_2$	Na_2S_4 Na_2S_2	94 57	10
3-$(CH_2)_4CONH_2$	$Cl(CH_2)_2CH(Cl)(CH_2)_4CONH_2$	Na_2S_2	83	10
3,3,5,5-$(CH_3)_4$-4-(=O)	$O{=}C[C(CH_3)_2Br]_2$	Na_2S_2	35	28

The disulphides to be cyclised are readily formed and are used without isolation in pure form, by the action of hydrogen sulphide on β-chlorosulphenyl-carboxylic acids, when cyclisation occurs sometimes spontaneously[29], and sometimes in the presence of an organic base[30]:

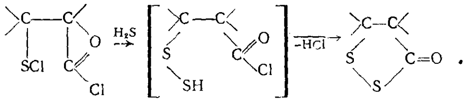
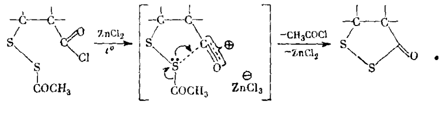


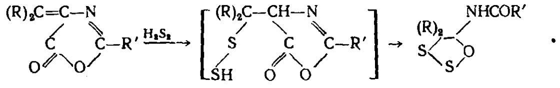
Table 3. Cyclisation of β-acetyldithio-carbonyl chlorides by zinc chloride[32].

1,2-Dithiolan-3-one	Unsubstituted	5-C_6H_5-	4-CH_3-	5-CH_3-	4-Cl-	4-Cl-4-CH_3
Yield, %	50	70	67	71	89	86

1,2-Dithiolan-3-ones are formed especially readily by intramolecular transacylation of the chlorides of β-acetyldithio-carboxylic acids (Table 3) catalysed by zinc chloride, with removal of acetyl chloride from the reaction zone[31,32]:



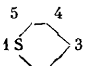
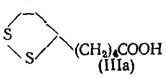
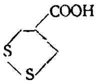
An example is the intramolecular transacylation of a 4-mercaptothiomethyl-1,3-oxazolin-5-one:[33]



2. Physical Properties

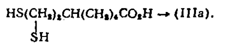
Crystallographic examination of the structure of 1,2-dithiolan-4-carboxylic acid has shown[10] that the molecule is non-planar and unsymmetrical. The angle between the $C_{(5)}-S_{(1)}-S_{(2)}$ and the $S_{(1)}-S_{(2)}-C_{(3)}$ planes is 26.6°—not the 90° found in open-chain disulphides[34]—which leads to repulsion of the unshared *p*-electrons of the sulphur atom and instability of the 1,2-dithiolan ring[35]. The angle at a sulphur atom is also smaller (92° instead of the 107° in linear disulphides)[36], so that the S−S bond is longer in 1,2-dithiolans than in open-chain disulphides (2.1 instead of 2.044 Å)[10].

Table 4.

1,2-Dithiolan	Stress, kcal $mole^{-1}$	Method of determination	Ref.
 (III)	14—18	calculation of deformation of bond angles	37
	27	from shift of λ_{max} in ultraviolet	10,38
	6.5	kinetic measurements of $C_6H_5CH_2SH$-(III) equilibrium	10,38
	4*	calorimetrically from heat of reaction**	10,39
 (IIIa)	3.5	calorimetrically from heat of reaction***	10,38
	11	crystallographic structure analysis	10,38
	16—30	conformational analysis	10,38

*The stress in 1,2-dithian determined by the same method was 0.5 kcal $mole^{-1}$.[38]

** $HS(CH_2)_3SH \xrightarrow{I_2} (III)$.

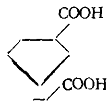
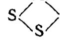
*** 

$HS(CH_2)_2CH(CH_2)_4CO_2H \rightarrow (IIIa)$ (SH on CH).

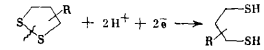
The stress in the 1,2-dithiolan ring has been determined by many workers using various methods (Table 4). Strongly divergent values have been obtained. The underestimates given by chemical methods may be due either to the presence of a polymer in the specimens or to the fact that the comparable reactions were conducted in solution, not in the vapour phase[10,37,38].

In conformity with the negative inductive effect of the disulphide group the measured dipole moments and the acidity of 1,2-dithiolan-4-carboxylic acids exceed those of cyclopentanecarboxylic acids (Table 4a)[39].

Table 4a.

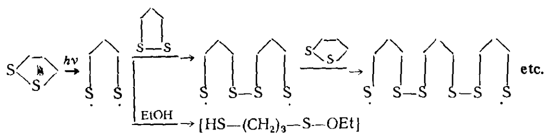
	μ, D	pK_a
	1.70	4.93
	3.15	3.82

1,2-Dithiolans are reduced polarographically (mostly at pH ~ 2.2) by a two-electron mechanism via intermediate mercury complexes to dithiols[10,40,41]:

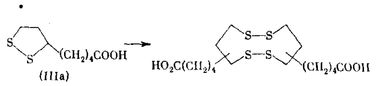


The half-wave potential $E_{1/2}$ is higher for 1,2-dithiolans than for linear and more macrocyclic disulphides[40,41].

On photolysis 1,2-dithiolans readily polymerise[42], and in alcohol they react with the solvent[35]:



Exposure of aqueous α-lipoic acid (IIIa) leads to rapid dimerisation[43]:

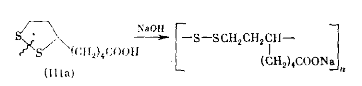


The ultraviolet spectra of 1,2-dithiolans have been studied ($\lambda_{max} \simeq 310-350$ nm).[36] In contrast to cyclic disulphides, polymeric linear disulphides absorb at 230 to 250 nm.[22] 1,2-Dithiolancarboxylic acids are exceptions, absorbing at 250−280 nm, with only weak absorption at 330 nm.[10] 1,2-Dithiolan-3-ones exhibit carbonyl absorption in the infrared (at 1710−1720 cm^{-1}).[32]

3. Chemical Properties

(*a*) Polymerisation

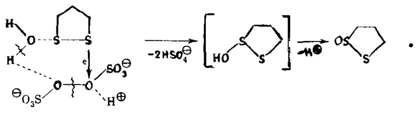
The most characteristic property of 1,2-dithiolans is their ease of polymerisation to linear disulphides, especially when heated or in the absence of a solvent, the activation energy of polymerisation being very low (8.6 kcal $mole^{-1}$).[36] All monosubstituted 1,2-dithiolans—the 4-amine[22], 3-carboxylic acid[44,45], methyl 3-carboxylate[41], 3-one[32], 4-one[24], and 4-hydroxymethyl derivative[46]—tend to polymerise, as well as certain disubstituted derivatives, 3,3-dimethyldithiolan[37] and the 4-methyl-3-valeric acid[23]. 3,3,5,5-Tetramethyl-1,2-dithiolan polymerises only in the presence of a catalyst (H^+, RS^-, OH^-, $AlCl_3$).[37] On addition of an aqueous alkali the compound (IIIa) also forms a polymer[47]:



(*b*) Reduction and oxidation

In the presence of zinc in hydrochloric acid[21], zinc in aqueous ammonia, sodium in liquid ammonia, and sodium tetrahydroborate[44,45], 1,2-dithiolans are readily reduced at the disulphide bond to 1,3-dithiols (Table 5).[10]

1,2-Dithiolans are more easily oxidised than are linear or macrocyclic disulphides[41]. Under controlled conditions both cyclic thiosulphinates (1-oxides) and thiosultones (1,1-dioxides) can be obtained (Table 6). Thiosultones are most stable compounds[41]. Oxidation with hydrogen peroxide more often gives 1-oxides, but 1,1-dioxides are formed when the ring contains electron-donor substituents or in the presence of a catalyst (Table 6). The oxidation of 1,2-dithiolans (e.g. by a persulphate) proceeds by a mechanism of one-electron transfer[20,36]:



The primary oxidation products of 1,2-dithiolans are thiosulphinates, which can then be oxidised further to 1,1-dioxides (Table 7).[20,49]

Table 5. Reduction of 1,2-dithiolans.

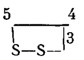
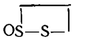
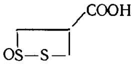
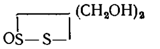
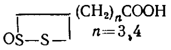
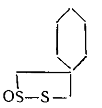
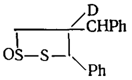
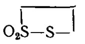
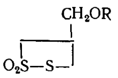
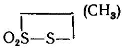
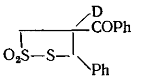
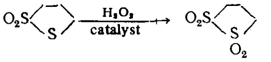
1,2-Dithiolan	1,3-Dithiol	Reagent	Yield, %
	$HS(CH_2)_3SH$	Zn, HCl	100
-4-COOH	$(HSCH_2)_2CHCOOH$	Zn, NH_4OH	—
-3,5-$(COOH)_2$	$HO_2CCH(SH)CH_2CH(SH)CO_2H$	Zn, HCl	90
-4-$(CH_3)_2$	$(CH_3)_2C(CH_2SH)_2$	Na, NH_3	94
-4-$(CH_2OH)_2$	$(HOCH_2)_2C(CH_2SH)_2$	Na, NH_3 H_2, CO_2S_x	87.5 71

Table 6. Oxidation products from 1,2-dithiolans.

1-Oxide	Oxidant (temp., °C)	Yield, %	Ref.
	H_2O_2 (75°)	76	11
	$NaIO_4$ H_2O_2 (5°)	— 72*	43 15
	H_2O_2 (t°)	77	39
	H_2O_2 or $(NH_4)_2S_2O_8$	—	19
	H_2O_2 (t)	76	39
	$NaIO_4$	86	45
1,1-Dioxide	**Oxidant (temp., °C)**	**Yield, %**	**Ref.**
	H_2O_2, tungstic acid (25°)	33	12
	H_2O_2 (75°)	16	16
	H_2O_2 (20°)	35	48
	m-ClC_6H_4COOH	good	49

*Mixture of *anti*- and *syn*-sulphoxides (in the proportions 77 : 23).[46]

1,2-Dithiolan 1,1-dioxide can be oxidised further by hydrogen peroxide in the presence of tungstic acid to the stable 1,1,2,2-tetroxide[12]:



(8%) .

Table 7. Products of the oxidation of 1,2-dithiolan 1-oxides.

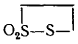
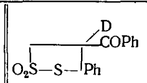
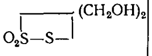
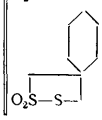
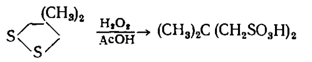
1,1-Dioxide	Reagent	Yield, %	Ref.	1,1-Dioxide	Reagent	Yield, %	Ref.
	H_2O_2	20	11		$R—CO_3H$	—	49
	H_2O_2, t°	54	39		H_2O_2	—	41

Table 8. Products of the cleavage of 1,2-dithiolan-3-ones by sulphuryl[50] or sulphenyl[51] chlorides.

Substituents	Reagent	Cleavage product	Yield, %
4-Methyl	SO_2Cl_2 PhSCl	$ClSSCH_2CH(CH_3)COCl$ $PhS_3CH_2CH(CH_3)COCl$	70 60
5-Methyl	SO_2Cl_2 CH_3SCl PhSCl	$ClSSCH(CH_3)CH_2COCl$ $CH_3S_3CH(CH_3)CH_2COCl$ $PhS_3CH(CH_3)CH_2COCl$	78 76 75
4-Chloro	SO_2Cl_2	$ClSSCH_2CH(Cl)COCl$	90
4-Chloro-4-methyl	SO_2Cl_2 CH_3SCl PhSCl	$ClSSCH_2C(CH_3)(Cl)COCl$ $CH_3S_3CH_2C(CH_3)(Cl)COCl$ $PhS_3CH_2C(CH_3)(Cl)COCl$	85 89 64

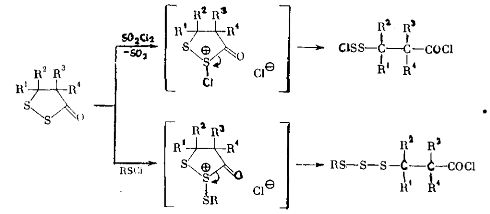
The oxidation of 4,4-bishydroxymethyl-1,2-dithiolan by hydrogen peroxide to the 1,1,2,2-tetroxide is usually accompanied by ring cleavage to give disulphonic acids[10]. Better yields of the latter are obtained from alkylated 1,2-dithiolans by the prolonged action of excess of potassium permanganate[41] or hydrogen peroxide[10]:



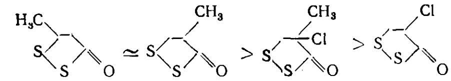
$(CH_3)_2C(CH_2SO_3H)_2$ (53%) .

(*c*) Reactions with electrophilic reagents

It has recently been shown that the chlorolysis of 1,2-dithiolan-3-ones by sulphuryl or sulphenyl chlorides involves selective cleavage of only the CO—S bond (Table 8)[50,51]:



These dithiolanones form the sequence



according to ease of rupture of the CO–S bond.

(*d*) Removal of a sulphur atom

A novel reaction of 1,2-dithiolans is the removal of a sulphur atom by trisdiethylaminophosphine[13,52] or triphenylphosphine[17,53] with the formation of four-membered heterocycles—thietans, β-thiolactones, and thietan-2,4-diones (Table 9). The process is a second-order reaction accompanied by inversion (S_N2), with intermediate formation of an internal phosphonium salt[13,52]:

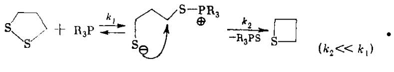
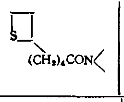
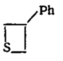
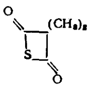
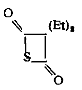
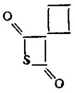
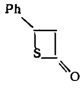
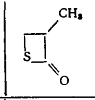
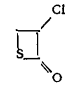


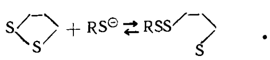
Table 9. Thietans from 1,2-dithiolans.

Thietan				
Reagent Temperature, °C Yield, % Reference	$(Et_2N)_3P$, 20—80° 82 13,52	$(Et_2N)_3P$, 20—80° 64 13,52	$(Et_2N)_3P$, 20—80° 87 13,52	Ph_3P, 60° 86 17

Thietan					
Reagent Temperature, °C Yield, % Reference	Ph_3P, 60° 83 17	Ph_3P, 60° 87 17	Ph_3P, 5—20° 98 53	Ph_3P, 5—20° 34 53	Ph_3P, 5—20° 24 53

(*e*) Reactions with metal alkyl sulphides and with inorganic salts

Thiols cleave 1,2-dithiolans very slowly:



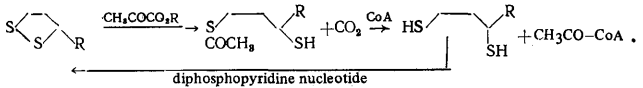
(III)

The rate of reaction increases in the presence of a weak base (the acetate ion)[10,54]. The rate of cleavage of the disulphide bond by sodium cyanide depends on the structure of (III). Thus unsubstituted (III) is cleaved rapidly and completely, the 3,3-dimethyl derivative slowly, and 3,3,5,5-tetramethyl-1,3-dithiolan does not react with sodium cyanide[10,37].

The antibiotic gliotoxin (IIIb), which contains a 1,2-dithiolan ring, is cleaved at the disulphide bond when heated with potassium sulphide[33]. With mercury(II) chloride and bromide substituted 1,2-dithiolans form crystalline adducts, but their nature is still obscure[10,55,56].

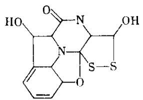
4. Biological Importance and Application

Of all the compounds containing a cyclic disulphide bond α-lipoic acid (IIIa) is the most important: it is a growth factor, and is involved in the oxidation of pyruvate and in photosynthesis[57]. In the organism reductive cleavage of (IIIa) gives a dithiol[58]:

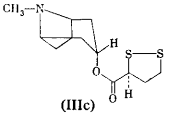


diphosphopyridine nucleotide
$R = (CH_2)_4COOH$ (III a)

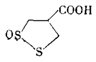
Gliotoxin (IIIb)—an antibiotic in which nitrogen atoms are attached to positions 3 and 4 of a 1,2-dithiolan ring—has an antitubercular and bacteriostatic action. 4-Acylamino-1,2-dithiolan-3-ones also possess tuberculostatic and cytotoxic activity[33]. 4-Amino-1,2-dithiolans are insecticidal[59]. 4-Dimethylamino-1,2-dithiolan—nereistoxin, isolated from marine worms—exerts a selective toxic action on harmful insects[60]. Intensive research is being conducted on its synthesis[22,61–63].



(IIIb)



(IIIc)



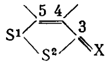
(IIId)

Bruguine—the tropinyl 1,2-dithiolan-3-carboxylate (IIIc) isolated from Cinchona—is an antitumour alkaloid[64,65]. 4-Hydroxy-1,2-dithiolan *trans*- and *cis*-1-oxides (brugierol and isobrugierol)[66], 1,2-dithiolan-3-carboxylic acid[67], and the 4-carboxylic (asparagusic) acid and its sulphoxide (IIId) also occur in plants; they inhibit the growth of lettuce, rice, radish, etc.[46,48]

All functionally substituted 1,2-dithiolans are potential protective agents against radiation[16].

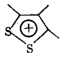
IV. 1,2-DITHIOLENS

Unsubstituted 1,2-dithiolen and its 3,3-disubstituted analogues are known. The 3-thiones (trithiones) (IVa), 3-ones (IVb), 3-imines (IVc), and 3-ylidenes (IVd) are discussed below.



(IV)

a) X=S c) X=NR
b) X=O d) $X=CR_2$



(V)

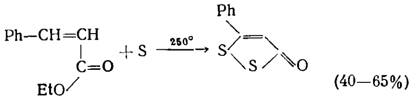
Several reviews have appeared on the chemistry of 1,2-dithiolium (V) salts[10,69,70], which therefore will not be considered in detail here. The literature on 1,2-dithiolens (IV) up to 1963 was examined in Breslow's monograph[10].

1. Methods of Preparation

(*a*) Sulphurisation of various types of organic compounds (with sulphur, phosphorus pentasulphide, and carbon disulphide)

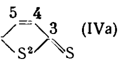
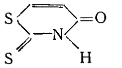
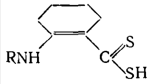
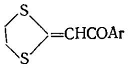
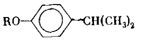
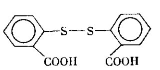
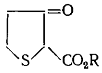
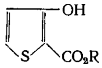
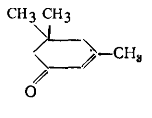
4,5-Dimethyltrithione was first obtained in 1884 by Barbagliya by the action of sulphur on isovaleraldehyde[10]:

Although the corresponding reaction with ethyl cinnamate gives 5-phenyl-1,2-dithiolen-3-one[71]



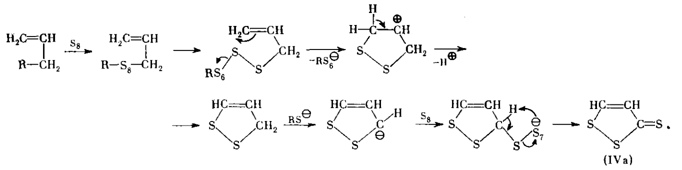
the *α*-methyl and *α*-ethyl-cinnamates yield the alkyl trithione-4-carboxylates or thiophens[10]. Sulphurisation of carbonyl (or thiocarbonyl) derivatives with sulphur and (or) phosphorus pentasulphide has so far remained the most general method for obtaining the 3-thiones (IVa), 3-ones (IVb), and 3-ylidenes (IVd) of 1,2-dithiolens (Table 10)[72-90]. The yields of trithiones from the reactions of hydrocarbons and halogenated hydrocarbons with sulphur (Table 11)[91-100] improve in the presence of basic catalysts (diphenylguanidine, mercury acetamide)[95].

Table 10. 1,2-Dithiolens by the sulphurisation of carbonyl and thiocarbonyl derivatives.

1,2-Dithiolen (IVa, b, d)	Reagent, condition.	Initial compound	Yield, %	Ref.
 (IVa)	S, P_2S_5, 135°	R—CO—CH=C(SR')$_2$ or (EtO)$_2$CHCH$_2$C(SEt)$_3$	47	72
	P_2S_5, C_5H_5N, t°		30	73
4,5-(Cl)$_2$-(IVb)	S, $AlCl_3$	CCl_2=CCl—COCl	48	74
4-R-(IVa)	P_2S_5, boiling xylene	$(CH_3S)_2$CHCH(R)CO$_2$Et	27—39	75
4-R-4-R'-(IVa)	P_2S_5, boiling xylene	R'—CS—CH(R)CO$_2$Et	31—60	75
4,5-(CH$_2$)$_4$-(IVa)	S, DMF, 20°		50	76
5-EtO$_2$C-(IVb)	S, t°	EtO$_2$C—CH=CH—CO$_2$Et	9	10
		$(CH_3S)_2$C=CHCOAr	87	10
5-Ar-(IVa)	P_2S_5, boiling xylene	(HS)$_2$C=CHCOAr	78	10
			96	10
4-R-5-Ar-(IVa)	S, 200°	Ar—CO—CR=C(SR)$_2$	1—6	77
	P_2S_5, boiling benzene		46	78
4-*p*-RO-C$_6$H$_4$-(IVa)	S, t°, catalysis		5—75	79
4,5-(—CH=CH—)$_2$-(IVb)	S, 300°		65	80
4-X-5-R-(IVa) (X=Cl, CN, CO$_2$Et)	P_2S_5, toluene	RCOCH(X)CO$_2$Et (X=Cl, CN, CO$_2$Et)	40—70	81
4-Ph-5-EtO$_2$C-(IVa)	P_2S_5	EtO$_2$C—CH(Ph)—CO$_2$Et	20	82
5-Ph-(IVa)+Z *	S, P_2S_5	Ph—CO—CH$_2$—C(NR$_2$)=NH	—	83
4-RCO-5-R'-(IVa)	S, 220°, PhCO$_2$Et	R—CO—C(CH$_3$)=CH—R'	20—38	84
4-ArCO-5-Ar'-(IVa)	S, 215°, PhCO$_2$Et	Ar—CO—C(CH$_3$)=CH—Ar'	45	10, 85
4-Ar'CH$_2$-5-Ar-(IVa)	S, P_2S_5, 200°		—	85
3-[=C(CO$_2$R)$_2$]-5-Ar-(IVd)	S, 250°	Ar—CH=CH—CH==C(CO$_2$R)$_2$	9—23	86
3-(=CHCOR')-5-R-(IVd) + Z	S, 200°	R—(CH=CH)$_2$—CO—R'	5—40	87
4-Ar-5-CH$_3$S-(IVa)	P_2S_5, xylene	$(CH_3S)_2$C=C(Ar)CO$_2$R	70—80	88
4-CH$_3$S-5-Ph-(IVa)	P_2S_5, t°	$(CH_3S)_2$C=C(SCH$_3$)COPh	45	10
4,5-(—CH=CH—S—)-(IVa)	P_2S_5, C_5H_5N	 or 	8	89
4.5-[—COCH$_2$C(CH$_3$)$_2$CH$_2$]-(IVa)++4.5-[CH$_2$COCH$_2$C(CH$_3$)$_2$—]-(IVa)+Z	S, 200—250°		—	90

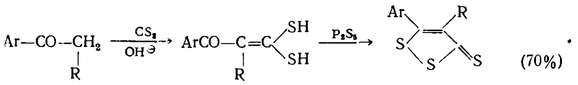
*Z represents a secondary product not containing 1,2-dithiolen.

The mechanism of the formation of trithiones (IVa) from alkenes[101] is



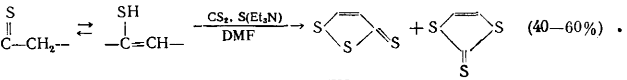
The use of phosphorus pentasulphide enables the temperature of this reaction to be lowered from 500° to 200°C.[91,92,101]

Sulphurisation of saturated and unsaturated hydrocarbons often produces difficultly separable mixtures of thiols, disulphides, thiophens, etc., so that the yields of (IV), especially from aliphatic compounds, rarely exceed 20% (Table 11). 5-Aryltrithiones are formed in higher yields, especially by the action of phosphorus pentasulphide on products of the condensation of aryl ketones with carbon disulphide (Table 10):[10,101]



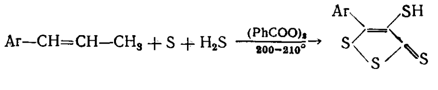
The action of sulphur and carbon disulphide in dimethylformamide on nitrogen-containing derivatives of hydrocarbons—ketimines, enamines, nitriles—also yields trithiones, together with isothiazolines (Table 12).[76,102-106]

With aliphatic thioketones (enethiols) carbon disulphide and sulphur give mixtures of isomeric 1,2-dithiolen-3-thiones (IVa) and 1,3-dithiolen-2-thiones[107]:

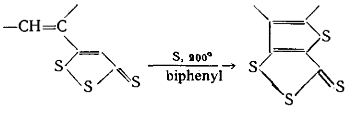


(IV a)

The sulphurisation of propenylbenzene in an atmosphere of hydrogen sulphide produces 4-mercaptotrithiones[10]:



In the presence of basic catalysts 5-alkenyltrithiones react with sulphur to form bicyclic thienotrithiones[108,109]:



(*b*) Cyclisation of derivatives of *β*-acetyldithio-carboxylic acids

Good yields of arylated and poor yields of alkylated 1,2-dithiolen-3-ones are obtained by the action of hydrogen chloride on *β*-acetyldithio-acrylic esters (in boiling methanol)[110].

When *β*-acetyldithio-*β*-chloro-carboxylic acids are heated in the presence of a zinc chloride catalyst without a solvent, high yields of alkylated and of halogenated

Table 11. Preparation of trithiones by the sulphurisation of hydrocarbons and halogenated hydrocarbons.

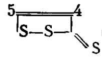
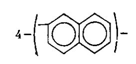
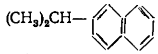
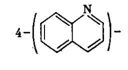
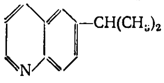
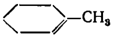
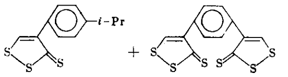
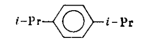
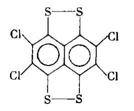
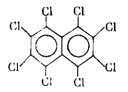
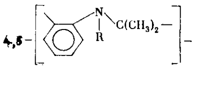
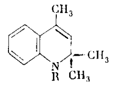
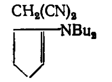
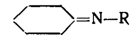
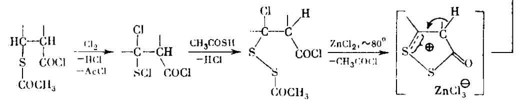
Trithione	Reagent, conditions	Initial compound	Yield, %	Ref.
 (IVa)	S, 550°, N_2	$CH_3—CH=CH_2$	56	91, 92
4-CH_3-	$S(SO_2)$, 195°	$(CH_3)_2C=CH_2$	39—42	10
4-Cl-	S, 500°, N_2	$CH_3—C(Cl)=CH—Cl$	44	93
4-F-		$CH_3—C(F)=CH_2$	46	93
4-CF_3-		$CH_3—C(CF_3)=CH_2$	46	93
4-CN-		$CH_2=C(CH_3)—CN$	19	93
4-C_6H_5-	S, 190—220°	$PhCX(CH_3)_2$ or $PhCH(CH_3)CH_2X$, or $PhCX(CH_3)CH_2X$, or $PhCHX(CH_3)CHX_2$ (X=Hal)	<40	94
4-Ar-	S, 190°, catalyst	$ArCH(CH_3)_2$	22—40	95
	S, 190°, catalyst		56	96
	S, 190°, catalyst		49	96
5-C_6H_5	S, 190—220°	$PhCHXCHXCH_2X$ or $PhCH_2CHXCH_2X$, or $PhCHXCH_2CH_3$, or $PhCH_2CHXCH_3$, or $Ph(CH_2)_3X$ (X=Hal)	11—18	94
4-C_6H_5-5-CH_3-	S, 190°, catalyst	$PhCH(CH_3)CH_2CH_3$	1	96
4-C_5H_5-5-HS-	S, DMF, t° (Me_2NH)	$(CH_3)_2CHPh$	52	97
4,5-$(C_6H_5)_2$-	S, 190°, catalyst	$PhCH_2CH(Ph)CH_3$	27	96
4,5-(—CH_2—$)_4$-	S, 130°		—	98
4,5-(—CH=CH—$)_2$-	S, 400°	Ph—CH_3	0.05	98
	S, 400—500°		—	91
	S, 320°, N_2		85	99
	S, t°		19—36	100

Table 12. Sulphurisation of nitrogen-containing compounds by a mixture of carbon disulphide and sulphur (in dimethylformamide at 20°C).

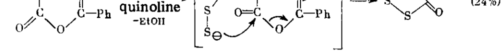
Trithione	Initial compound	Yield, %	Ref.
4-C_2H_5-	Et—CH=$CHNR_2$	50	102
4-C_6H_5-	PhCH=CH—NR_2	30	102
5-C_6H_5-	$CH_2=C(Ph)NR_2$	30	102
4-OCH_3-5-NH_2	NC—CH_2—$CO_2CH_3^*$	38	103
4,5-$(NH_2)_2$-	NC—$CH_2CONH_2^*$	27	103
4-CN-5-NH_2	$CH_2(CN)_2$	70	104
4,5-(—CH_2—$)_3$-		60	105
4,5-(—CH_2—$)_4$-		30—40	76
4,5-(—CH_2—$)_n$- + Z **; n=3—5	CH=C—NR_2 ( ) $(CH_2)_n$ n=3.5	30—50	102, 106

*Reaction with carbon disulphide in presence of sodium methoxide.
**Z represents a secondary product.

1,2-dithiolen-3-ones are obtained, and even of the unsubstituted carbonyl compound (Table 13):[32]



4-Acylamino-1,2-dithiolen-3-ones are obtained by the reaction of 4-ethoxymethylenoxazol-5-one with hydrogen sulphide and sulphur in the presence of quinoline[111]:



(*c*) Other methods

The condensation of disulphane with derivatives of phenylpropionic acid during exposure to ultraviolet radiation gives 5-phenyl-1,2-dithiolens (this reaction cannot be accomplished with the aliphatic analogues)[10]:

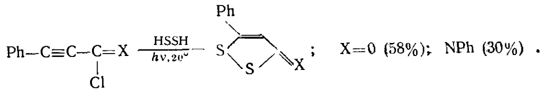
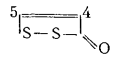
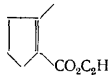
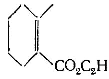
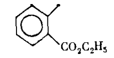
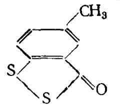
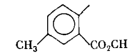
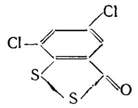
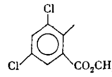
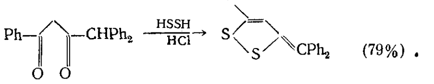


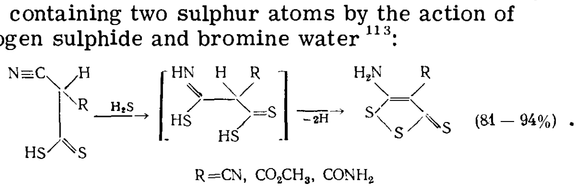
Table 13. Cyclisation of derivatives of β-acetyldithiocarboxylic acids CH_3COSSR by methanolic hydrogen chloride[110] or by zinc chloride[32].

1,2-Dithiolen-3-one	R	Yield, %	Ref.
	$CHClCH_2COCl$	87	32
4-CH_3-	$CHClCH_2(CH_3)COCl$	92	32
5-CH_3-	$CCl(CH_3)CH_2COCl$	90	32
5-CH_3	$C(CH_3)=CHCO_2C_2H_5$	20	110
4-Cl-	$CHClCHClCOCl$	68	32
4,5-$(CH_3)_2$-	$C(CH_3)=C(CH_3)CO_2C_2H_5$	17	110
5-C_6H_5-	$C(Ph)=CHCO_2C_2H_5$	80	110
5-(p-C_6H_4)-	$C(p\text{-}CH_3C_6H_4)=CHCO_2C_2H_5$	76	110
5-(p-Cl-C_6H_4)-	$C(p\text{-}Cl-C_6H_4)=CHCO_2C_2H_5$	81	110
4,5-$(CH_2)_3$-		9	110
4,5-$(CH_2)_4$-		30	110
4,5-$(CH=CH)_2$-		95	110
		88	110
		76	110

The reaction of disulphane with arylated 1,3-diketones yields 1,2-dithiolylidene compounds[112]:



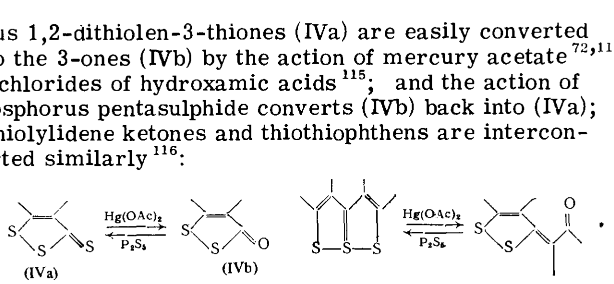
5-Aminotrithiones are formed from α-cyano-carboxylic acids containing two sulphur atoms by the action of hydrogen sulphide and bromine water[113]:



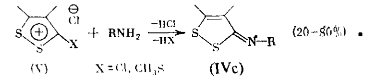
R=CN, CO_2CH_3, $CONH_2$

(*d*) Interconversion of 1,2-dithiolen derivatives

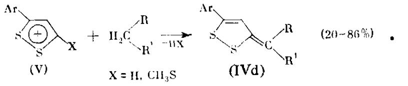
1,2-Dithiolens themselves are often the starting materials for obtaining other compounds of this type. Thus 1,2-dithiolen-3-thiones (IVa) are easily converted into the 3-ones (IVb) by the action of mercury acetate[72,114] or chlorides of hydroxamic acids[115]; and the action of phosphorus pentasulphide converts (IVb) back into (IVa); dithiolylidene ketones and thiothiophthens are interconverted similarly[116]:



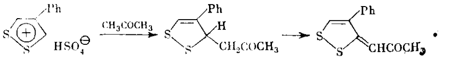
1,2-Dithiolen-3-imines (IVc) are obtained by the reaction of 3-chloro- or 3-methylthio-1,2-dithiolium salts (V) with amines[117-120] or with *NN*-dichlorobenzamides[121], the yield of (IVc) depending on the basicity of the amine:



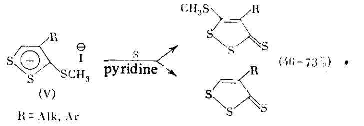
1,2-Dithiolylidenes (IVd) are usually obtained by condensing 1,2-dithiolium salts (V) with compounds containing active methylene groups[122-124]:



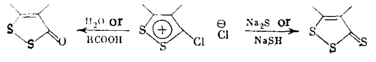
However, the reaction of a 4-phenyl-1,2-dithiolium salt with acetone gives a stable 3-monosubstituted 1,2-dithiolen, which forms a dithiolylidene ketone (IVd) only in the presence of chloranil[125,126]:



Sulphur acts on 1,2-dithiolium salts under mild conditions to form trithiones; in the case of 3-methylthio-1,2-dithiolium salts (V) this reaction gives a mixture of the expected 5-methylthiotrithione and a trithione formed by demethylation of the initial compound (V):[127-129,159]



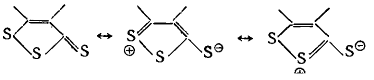
More nucleophilic bases convert 3-chloro-1,2-dithiolium salts into trithiones, and the less nucleophilic bases yield 1,2-dithiolen-3-ones[74,130]:



2. Physical Properties

1,2-Dithiolens have a planar *cis*-configuration of the disulphide bond, which would appear to be energetically less favourable than in 1,2-dithiolans, and still less than in open-chain disulphides (dihedral angle between the planes of the valencies of the sulphur atoms respectively 0°, 27°, and 90°). Actually, however, unsaturated five-membered cyclic disulphides are far more stable than the saturated rings, because the energy of repulsion of the unshared *p* electrons of the sulphur atoms is balanced by the conjugation energy of *p* and π electrons[34].

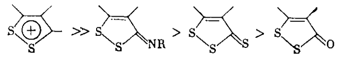
The structures of trithione[131] and 4-methyltrithione[132] have been established by means of X-rays. The molecules are planar[10], with carbon–carbon and carbon–sulphur bond lengths closely similar to those in benzene and in thiophen, but the sulphur–sulphur bond length in trithiones (2.04 Å) is identical with that in S_8 and R_2S_2 molecules. The structure of trithiones is therefore a hybrid of the resonance structures



in the proportions 5 : 4 : 1.[133]

According to LCAO-MO calculations, trithione and its 4- and 5-phenyl analogues have a low π-order of the S–S bond (0.07–0.08,[133] 0.242 [34]) and a higher order of the $C_{(4)}-C_{(5)}$ π-bond (~0.8).[134] In contrast to the $C_{(3)}$ and $C_{(5)}$ atoms the $C_{(4)}$ atom of trithiones bears a fractional negative charge (about −0.06).[133,134] The considerable negative charge on the exocyclic sulphur atom (about −0.28) is explained by the tendency of trithione to acquire an aromatic configuration by repelling the "spare" π-electron[133].

1,2-Dithiolen-3-ones and -thiones are analogues of the non-alternant tropone and tropothione systems. A clear comparison of the aromaticities of the various types of 1,2-dithiolens (IVa–c) and (V) can be obtained from their energies calculated by the LCAO-MO method (Table 14).[134] According to their *DE/n* values these compounds form the sequence of diminishing aromaticity



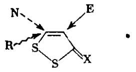
(V) (IVc) (IVa) (IVb)

Table 14. Energies of 1,2-dithiolens (in β-units)*.

No.	System	*n*	*DE*	*W*	*DE/n*
(IVb)	1,2-Dithiolen-3-one	8	1.063	12.527	0.133
(IVc)	1,2-Dithiolen-3-imine	8	1.096	10.332	0.137
(IVa)	1,2-Dithiolen-3-thione	8	1.057	9.425	0.132
(V)	1,2-Dithiolium ion	6	1.57÷2.05	7.57÷8.13	0.198÷0.342

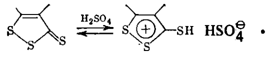
**DE* = delocalisation energy; *n* = number of π-electrons; *W* = total π-electron energy.

From the molecular diagrams for (IVa–c) it is predicted that centres of electrophilic, nucleophilic, and radical reactivity—*E*, *N*, and *R*—will have the locations[134]

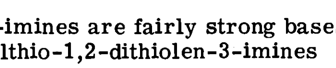


(IVa–c) (X = S, O, NR)

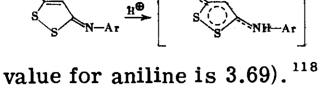
Because of the high electron density on the thiocarbonyl sulphur atom (1.576,[135] 1.433 [134]) trithiones exhibit basic properties and dissolve readily in acids[135]:



Protonation of the less basic 1,2-dithiolen-3-ones leads to a greater proportion of the oxonium form than of the 1,2-dithiolium structure (according to ^{1}H-n.m.r. data)[70,136]:

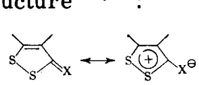


1,2-Dithiolen-3-imines are fairly strong bases. Thus for *N*-aryl-5-methylthio-1,2-dithiolen-3-imines



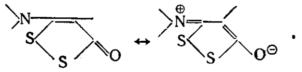
pK_b = 2.57 (the value for aniline is 3.69).[118]

Both trithiones and 1,2-dithiolen-3-ones have considerable dipole moments, although higher for similarly substituted trithiones because of the greater importance of the limiting polar structure[137,138]:



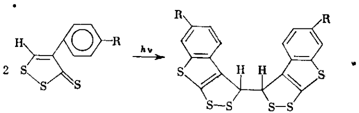
X = S, O .

Thus the measured dipole moments of the two groups lie in the ranges 3.3–5.5 and 2.8–4.9 D. The measured "apparent" conductivities are also higher for the former than for the latter group ($10^{15}\kappa$ is respectively 8.3–52 and 2.6 to 30 ohm^{-1} cm^{-1}).[137] The calculated dipole moment of unsubstituted trithione is 5.25 D.[133] 4-Halogeno- and 5-aryl-1,2-dithiolens have higher dipole moments than the corresponding 5-halogenated and 4-arylated compounds[138]. 1,2-Dithiolen-3-ones containing a tertiary amino-group at position 5 have extremely high dipole moments (4.74 to 6.73 D):[137,138]



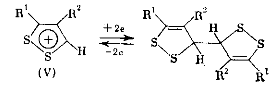
The surprisingly high melting points of trithiones[10] may be due to their high polarity.

The photochemical behaviour of 1,2-dithiolens is influenced by the position of the substituent. Whereas 5-phenyltrithione is photochemically stable[139], 4-*p*-tolyl- and 4-phenyl-trithiones undergo photochemical reactions at the C=S bond[140]:



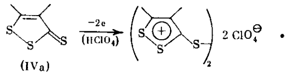
R = H (40%); CH_3 (44%)

1,2-Dithiolium ions (V) and bi-1,2-dithiolen-3-yls are interconverted electrochemically at a platinum electrode in acetonitrile[141]:



(V)

The preparative anodic oxidation of trithiones (IVa) yields bis-1,2-dithiolium disulphide[142]:



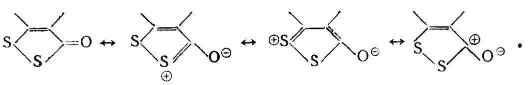
(IVa)

Trithiones are oxidised at potentials of ~0.8–1.32 V, and 1,2-dithiolium salts are reduced between about +0.32 and −0.06 V. Substituents in the ring affect both oxidation and reduction potentials: monosubstituted derivatives are oxidised and reduced far more easily than are disubstituted derivatives[142]. Polarographic reduction of trithiones gives a cathodic wave having a half-wave potential of −0.9 V.[101]

Ultraviolet and visible spectra. Trithiones exhibit strong absorption bands at 225, 250, 280, 335, and 417 nm,[101] which are somewhat displaced in the arylated compounds[10].

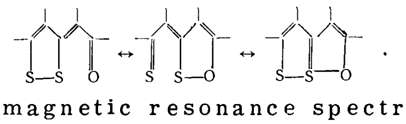
Infrared spectra. The 1,2-dithiolen framework shows characteristic absorption bands at 504–561 and 1508–1567 cm^{-1} (sulphur–sulphur and carbon–carbon vibrations of the ring)[143]. Later results reveal characteristic infrared lines at 405–420 and 430–450 cm^{-1} (planar deformation vibrations of the ring) and at 1305 to 1350 and 1490–1565 cm^{-1} (stretching vibrations of the ring). Sulphur–sulphur stretching vibrations of 1,2-dithiolens[144] appear at 480–525 cm^{-1}.

1,2-Dithiolens-3-ones exhibit a low carbonyl frequency (1610–1685 cm^{-1}),[32,115] like their analogue tropone (1638 cm^{-1}), as a consequence of the electron displacement[138,144]

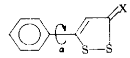


(IVb)

Therefore (IVb) with a tertiary amino-group at position 5 have the lowest carbonyl frequency (1610–1635 cm^{-1}).[138] The thiocarbonyl group in trithiones[115] absorbs at 1110 to 1190 cm^{-1}. The carbonyl frequency of α-1,2-dithiol-3-ylidene ketones is located in a very low range (1550–1600 cm^{-1}), owing to interaction of the carbonyl oxygen with a cyclic sulphur atom[145,146]:



Proton magnetic resonance spectra. The signals of the ring protons, especially the fragment =CH–S, in 1,2-dithiolen-3-ones and -thiones are situated down-field (δ ≃ 6.3–8.4 p.p.m.) from those for cycloalkenes (for cyclopentene δ_{CH} = 4.4 p.p.m.), owing to conjugation of the carbonyl (or thiocarbonyl) group and the heteroatoms[32,147]. The chemical shifts of the aromatic protons in 5-aryl-1,2-dithiolens indicate that the rings are non-coplanar



X=O, S;

with the preferred deformation α = 30°. The electron-acceptor inductive contributions found experimentally for 1,2-dithiolens with respect to the aryl substituent are −0.13 and −0.16 according as X = O or S.[148]

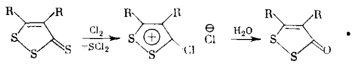
Mass spectra. 1,2-Dithiolens exhibit an intense peak due to the molecular ion, which may also indicate the aromaticity of these compounds[149,150].

3. Chemical Properties

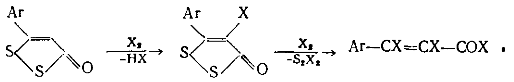
Trithiones are more reactive than 1,2-dithiolen-3-ones because of the greater polarisability of the thiocarbonyl group[151].

(*a*) Reactions with electrophilic reagents

Under mild conditions alkylated 1,2-dithiolen-3-thiones react readily with chlorine only at the thiocarbonyl bond to form a dithiolium salt, which is easily converted by interaction with the solvent (water, acetic acid) into the corresponding 1,2-dithiolen-3-one:[74,80,152,153]



As the system becomes more strongly aromatic, the ring also undergoes chlorination: the halogenation of 4-arylated or (under more severe conditions) 5-arylated 1,2-dithiolen-3-thiones, for example, yields the corresponding 5- or 4-halogenated 3-ones.[10,120,154,155] Under still more severe conditions (prolonged action of excess of halogen in boiling tetrachloromethane), however, substitutive halogenation is accompanied by ring cleavage with loss of both sulphur atoms and formation of the corresponding derivatives of αβ-dihalogenocinnamic acids[156,157]:



X=Cl, Br

Even under mild conditions unsubstituted and alkylated 1,2-dithiolen-3-ones undergo only ring fission with sulphuryl chloride, sulphenyl chlorides, and chlorine, at the S–CO bond with the chlorides and at both S–CO and S–S bonds with chlorine (Table 15):[50,51]

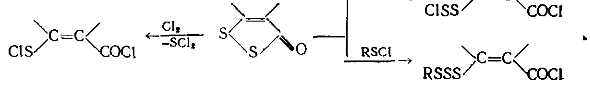
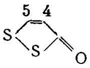
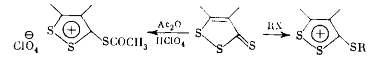


Table 15. Products of the cleavage of 1,2-dithiolen-3-ones by SO_2Cl_2,[50] RSCl,[51] and Cl_2.[50]

1,2-Dithiolen-3-one	Reagent	Product	Yield, %
	SO_2Cl_2 Cl_2 CH_3SCl C_6H_5SCl	ClSSCH=CHCOCl ClSCH=CHCOCl CH_3S_3CH=CHCOCl $C_6H_5S_3CH$=CHCOCl	50 72 43 83
4-Methyl-	SO_2Cl_2	ClSSCH=C(CH_3)COCl	68
5-Methyl-	SO_2Cl_2	ClSSC(CH_3)=CHCOCl	79

(*b*) Formation of 1,2-dithiolium salts

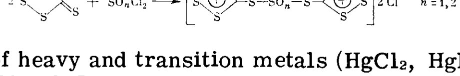
Alkylated[10,135,158–160] and acylated[105] trithiones usually yield 1,2-dithiolium salts:



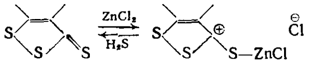
X = I, Br, Cl, HSO_4, HgI_3 etc.
R = Alk, CH_2COR[158] etc.

1,2-Dithiolen-3-ones react similarly with acetic anhydride[105] and with triethyloxonium fluoroborate[161,162]. Trithiones are converted into 3-chloro-1,2-dithiolium salts by the action of oxalyl chloride, trichloromethyl isocyanide dichloride, or thiocarbonyl chloride ten times as easily as are 1,2-dithiolen-3-ones[105,151]. These salts are formed also from 1,2-dithiolen-3-ones and phosphorus pentachloride or phosphoryl chloride[80,163], but not with phosphorus trichloride or thionyl chloride[80].

Under mild conditions trithiones form 2 : 1 ionic adducts with oxalyl[80], thionyl, or sulphuryl[101,164] chloride:



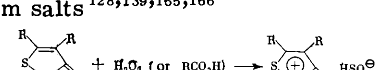
Halides of heavy and transition metals ($HgCl_2$, $HgBr_2$, HgI_2, $CdCl_2$, CdI_2, $ZnCl_2$, $FeCl_3$, $AgNO_3$, $SbCl_3$, $CuCl_2$, Cu_2Br_2, $AuCl_4$, $PdCl_2$, $PtCl_4$, $BiCl_3$, and $SnCl_4$) form with trithiones yellow crystalline complexes (1 : 1 or 1 : 2) also involving the thiocarbonyl group[10,101]:



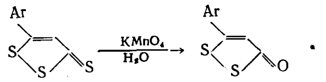
Trithiones form with 1,2-dithiolen-3-ones 1 : 2 donor–acceptor complexes[164].

(*c*) Oxidation and reduction

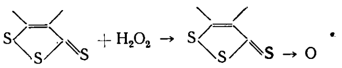
Oxidising agents convert alkylated trithiones into 1,2-dithiolium salts[128,139,165,166]



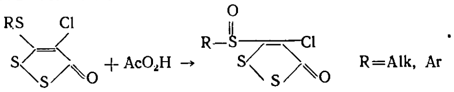
and arylated trithiones into 1,2-dithiolen-3-ones[120]



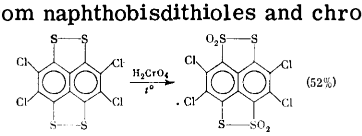
Trithiones can sometimes be oxidised to trithione *S*-oxides[167,168]:



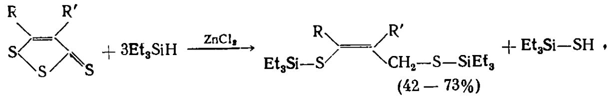
5-Alkyl(and aryl)thio-1,2-dithiolen-3-ones are oxidised only at the exocyclic sulphur atom with the formation of sulphinyl derivatives[118,169]:



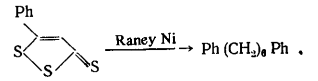
Heating with chromic and nitric acids oxidises 4,5-dimethyltrithione to acetic acid, and 5-*p*-methoxyphenyltrithione to anisic acid[101]. The only known example of oxidation of a dithiole sulphur atom is the formation of thiosultones from naphthobisdithioles and chromic acid[99]:



The reduction of trithiones by triethylsilane involves both thiocarbonyl and disulphide bonds[170]:

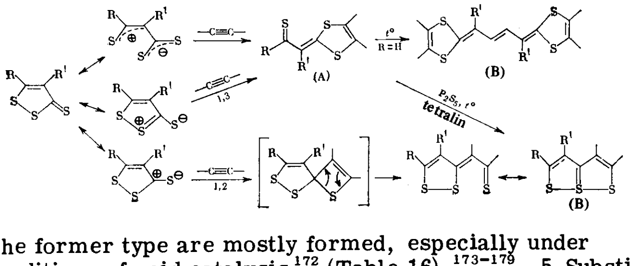


Sulphur is completely removed when trithiones undergo hydrogenation in the presence of Raney nickel, and the hydrocarbon residues dimerise[101]:



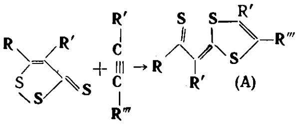
(*d*) Condensation

Alkynes. The discovery in 1964 of the reaction of trithiones with alkynes showed[171] that, depending on the reaction conditions and the nature of the substituents, the trithiones can react in one of the possible resonance structures, with the formation of compounds of types (A) and (B):



The former type are mostly formed, especially under conditions of acid catalysis[172] (Table 16).[173–179] 5-Substituted thiones are more reactive[171]. In the absence of a 5-substituent thioaldehydes (A: R = H) are formed; these are unstable, and when heated readily lose sulphur with the formation of biadducts of type (C).[174,179] In the absence of acids either a mixture of isomeric compounds (A) and (B) or solely (B) is produced (Table 17).[172–180] The isomers differ in their ultraviolet spectra[177]. 1,3-Dithiolylidene thioketones (A) are easily isomerised to thiothiophthens (B) by heating with phosphorus pentasulphide[176].

Table 16.

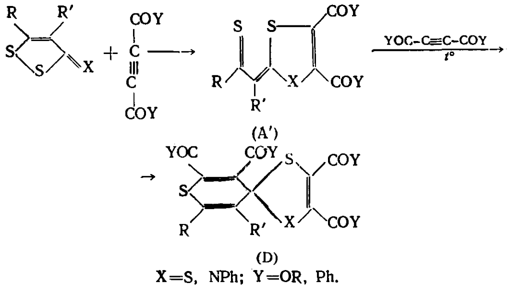


R	R′	R″	R‴	Conditions,°C	Yield of (A), %	Ref.
Ph	H	CO_2Me	CO_2Me	20°	82	173—176
				dioxan, $t°$	82	177
Ph	H	CO_2Et	CO_2Et	$CHCl_3$, $t°$	84	175, 177
Ph	H	H	CHO	20°	92	175, 177
Ph	H	Ph	H	xylene, $t°$	42	175, 177
				xylene, HCl, $t°$	30	172, 176
Ph	H	H	p-O_2N—C_6H_4	dioxan, $t°$	39	175, 177
Ph	H	$CONH_2$	$CONH_2$	80°	81	177
Ph	H	CO_2Et	Ph	dioxan, $t°$	75, 92	174, 175, 177
Ph	H	PhCO	Ph	dioxan, $t°$	79	177
Ph	H	CO_2Et	CH_3	benzene, $t°$	74	174
Ph	H	CH=CH—CH=CH		benzene, $t°$	28	173
»	»			catalyst, $Pb(OAc)_4$	55	174
Ph	Ph	CO_2Et	Ph	$t°$	56	176
p-Br-C_6H_4	H	Ph	H	HCl	25	
p-Cl-C_6H_4	H	H	Ph	dioxan, $t°$	52	177
		CO_2Me	CO_2Me	dioxan, $t°$	75	177
		H	p-$CH_3OC_6H_4$	toluene, $t°$	58	177
Ph	p-$CH_3OC_6H_4CO$	CO_2Me	CO_2Me	$CHCl_3$, $t°$	73	177
H_2N	CN	CO_2Me	CO_2Me	DMF, $t°$	44	177
		H	Ph	DMF, $t°$	40	177
$CH_2CH_2CH_2$		CO_2H	H	60°	90	177
		CO_2Et	Ph	130°	40	177
		PhCO	Ph	toluene, $t°$	82	177
CH_3S	Ph	H	SCH_3	140°	43	178
H	Ph	CO_2Me	CO_2Me	—	85	179
CH_3CH_2	CH_3	CO_2Me	CO_2Me	—	65	174
H	H	CO_2Me	CO_2Me	20°	74	179
		PhCO	PhCO	20°	70	
		$CO_2H(CO_2Me)$	H	—	60	92

The reactivity of acetylenic compounds in these condensations falls in the sequence[175,176]

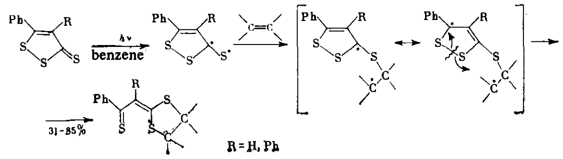
$$RO_2C—C{\equiv}C—CO_2R > HC{\equiv}C—CO_2R > Ar—C{\equiv}C—CO_2R > Ar—C{\equiv}C—H > Ar—C{\equiv}C—Ar\,.$$

Acetylenedicarboxylic esters are able to form not only 1 : 1 (A′) but also 2 : 1 (D) adducts or their mixtures in proportions depending on the reactivity of the alkyne and the temperature (Table 18):[173,174,176]



X=S, NPh; Y=OR, Ph.

Alkenes. Trithiones react with alkenes, in contrast to alkynes, only on irradiation, forming equimolecular adducts. Whereas 5-phenylated trithiones give 1,3-cycloaddition products with cleavage of the cyclic disulphide bond[181]



the 4-p-tolyl derivatives form adducts in which the ring remains intact[140]

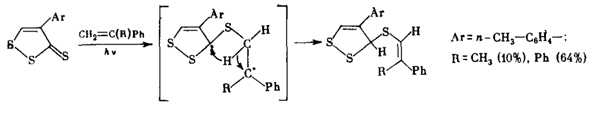
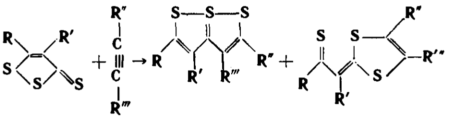
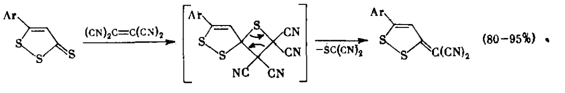


Table 17.



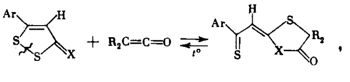
R	R′	R″	R‴	Conditions	Yield, % (B)	Yield, % (A)	Ref.
Ph	H	Ph	H	xylene, $t°$	30	0	172, 176
		p-Cl-C_6H_4	H	xylene, $t°$	5	10	176, 180
		p-Br-C_6H_4	H	xylene, $t°$	20	15	176, 180
		Ph	Ph	DMF, $t°$	41	0	177
		p-$CH_3OC_6H_4$	H	xylene, $t°$	48	0	180
p-$CH_3OC_6H_4$	H	Ph	H	xylene, $t°$	50	0	172, 176
		Ph	H	xylene, HCl, $t°$	10	60	172, 176
p-Br-C_6H_4	H	Ph	H	xylene, $t°$	20	20	176
p-$CH_3OC_6H_4$	CH_3	Ph	H	xylene, $t°$	50	0	176
				xylene, HCl, $t°$	15	15	176
Ph	CH_3	Ph	H	xylene, HCl, $t°$	20	10	176
				xylene, $t°$	50	0	176
p-Cl-C_6H_4	H	Ph	H	xylene, $t°$	25	25	176
CH_3S	CH_3	CH_3S	H	140°	42	0	178
CH_3S	p-$CH_3C_6H_4$	CH_3S	H	140°	38	0	178

The condensation of 5-aryltrithiones with the electron-deficient tetracyanoethylene does not require exposure[182]:



In contrast to trithiones, 1,2-dithiolen-3-ones do not react with alkynes and alkenes[175,181].

Ketens. 1,2-Dithiolens containing exocyclic C=S, C=O, and C=NR double bonds react readily in the cold with ketens—more reactive unsaturated compounds—to form equimolecular addition products. However, this reaction is reversible, and at higher temperatures the adducts break down into the initial components[111,183–185]:



R = H, CH_3; X = S (30–70%); O (40%); NPh (65–90%)

Certain adducts rearrange into 1,2-dithiolylidenes on standing[112,184]:

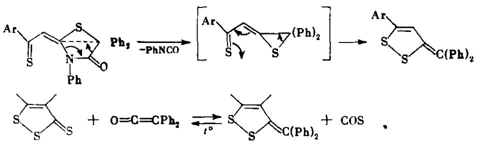
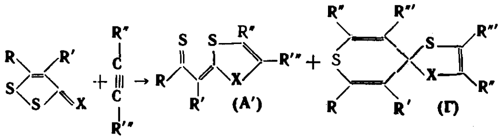
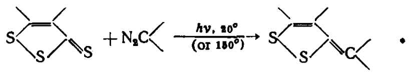


Table 18.

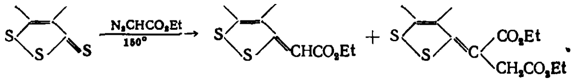


R	R′	X	R″	R‴	Conditions	Yield, % (A′)	Yield, % (D)	Ref.
Ph	H	NPh	CO_2Et	H	—	75	0	176
Ph	H	NPh	CO_2Et	Ph	—	64	0	176
Ph	H	NPh	CO_2Me	CO_2Me	—	0	63	176
Ph	Ph	NPh	CO_2Me	CO_2Me	heat	0	75	176
Ph	H	S	CO_2Me	CO_2Me	20°	43	44	174
					heat	0	93	173, 174, 176
Ph	H	S	COPh	COPh	—	71	14	179
Ph	Ph	S	CO_2Me	CO_2Me	20°	70	0	173, 174, 176
			ditto	ditto	heat	0	66	173, 174, 176
Ph	Ph	S	H	CO_2Et	heat	29	70	176
—$(CH_2)_3$—		S	CO_2Me	CO_2Me	—	78	9.5	174
—$(CH_2)_4$—		S	CO_2Me	CO_2Me	—	17	56	174
CH_3CH_2	CH_3	S	CO_2Me	CO_2Me	excess of reagent	0	96	174

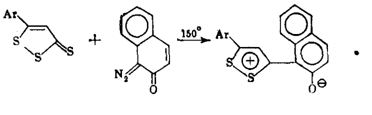
Carbenes and nitrens. Trithiones react extraordinarily readily with carbenes. Thus with diazoketones and with diphenyldiazomethane 1,2-dithiolylidenes are formed with loss of the thiocarbonyl sulphur[186]:



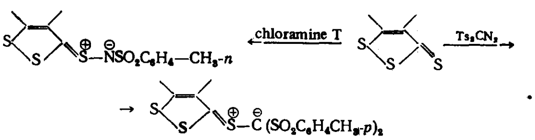
A mixture of 1 : 1 and 1 : 2 adducts is formed with the more reactive ethyl diazoacetate[186]:



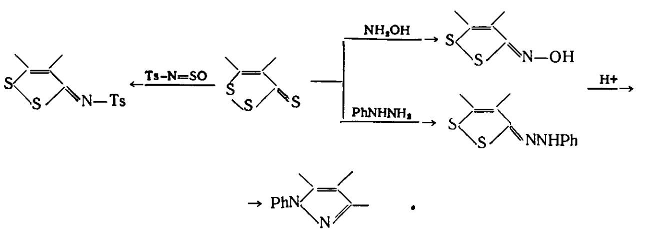
1-(1,2-Dithiolio)-2-naphthoxides are obtained from 1-diazodihydronaphthalen-2-one[186,187]



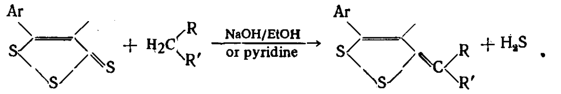
In some cases the thiocarbonyl group is preserved in the reaction of 4-phenyl- and benzo-trithiones with carbenes and nitrens. For the first time good yields have been obtained of stable thiocarbonyl ylides and their nitrogen analogues—imines[188]:



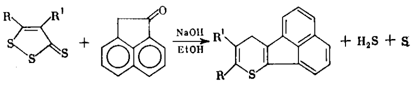
Hydroxylamine[10,189,190], phenylhydrazine[101], and *N*-sulphinyltoluene-*p*-sulphonamide[191]. Like ketones and thioketones, 1,2-dithiolen-3-thiones and -ones condense with these compounds to form the corresponding 3-imine derivatives. Phenylhydrazones are readily converted into pyrazoles[101]:

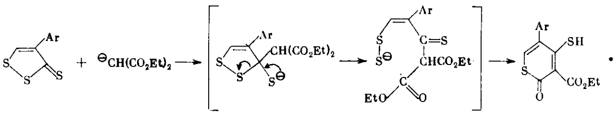


CH-Acids. Like thioketones, 5-aryltrithiones react readily with CH-acids—malononitrile, acenaphthenone, and malonic and cyanoacetic esters[101,192]—and with α-bromo-ketones[160] to form 1,2-dithiol-3-ylidenes[10,101]:

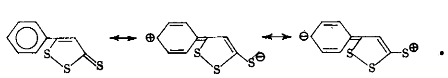


In contrast to the 5-aryl derivatives, the reaction of other trithiones with CH-acids usually involves cleavage of the ring[10,101,192]:

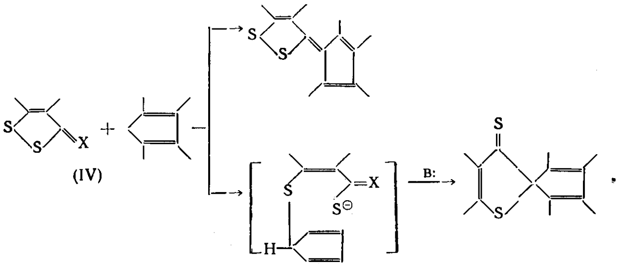




The great stability of 5-aryltrithiones towards cleavage is attributed to resonance stabilisation, which is impossible with the 4-aryl compounds:

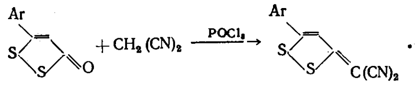


1,2-Dithiolen-3-thiones, -ones, and -ylidenes (IV) give with tetraphenylcyclopentadiene (or fluorene) in an alkaline medium a mixture of condensation and ring-cleavage products—dithiafulvalenes and spiro-compounds[123]:



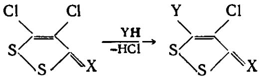
X=S, O, C(CN)2

In contrast to 5-aryl-1,2-dithiolen-3-thiones, the 3-ones can be condensed with malononitrile in the presence of phosphoryl chloride[125]:



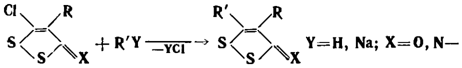
(*e*) Substitution with preservation of the ring

Numerous reactions of 5-chloro- and 4,5-dichloro-1,2-dithiolen-3-ones and -imines have shown that the 5-halogen is very easily substituted by any nucleophile[193–198], but a 4-halogen is not replaced even with excess of a nucleophile[196] (Tables 19–21):[118,120,121,170,193–197]

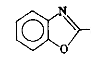
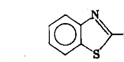
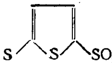
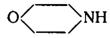
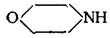


X=O, NR; Y=RS, RSO₂, RO, R₂N, RO—C(=S)—S, NH₂—C(=NH)—S etc.

Table 19. Reaction of 5-chloro-1,2-dithiolens with thiols, sulphinates, alkoxides, and amines:

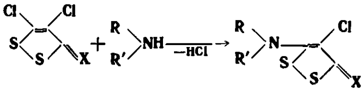


Y=H, Na; X=O, N—

X	R	R'Y	Yield, %	Ref.
O	Ph	CH_3SH	45	118
O	Ph	EtSH	25	118
O	Ph		36	118
O	Ph		37	118
N-SO_2—C_6H_4—CH_3-*p*	Cl	PhSH	72	193
N-CO_2Et	Cl	PhSH	62	193
N-SO_2—Ph	Cl	CH_3ONa	76	193
N-SO_2—C_6H_4—CH_3-*p*	Cl	CH_3ONa	66	193
N-CO_2Et	Cl	CH_3ONa	66	193
N-SO_2—Ph	Cl	*p*-CH_3—C_6H_4—SO_2Na	94	193
N-CO_2—Et	Cl	*p*-CH_3—C_6H_4—SO_2Na	82	193
N-CH_3	Cl	*p*-CH_3—C_6H_4—SO_2Na	47	193
N-CO—C_6H_4—NO_2-*o*	Cl	$PhSO_2Na$	77	121
N-CO—$C_6H_3(NO_2)_2$-*o*, *p*	Cl	$PhSO_2Na$	76	121
O	Cl	CH_3SO_2Na	70	118
O	Cl	$EtSO_2Na$	84	118
O	Cl	$(CH_3)_2CHSO_2Na$	61	118
O	Cl	$ClCH_2SO_2Na$	55	118
O	Cl	$PhSO_2Na$	97	118
O	Cl	*p*-CH_3—C_6H_4—SO_2Na	92	118
O	Cl	*p*-Cl—C_6H_4—SO_2Na	89	118
O	*p*-CH_3—C_6H_4		57	118
O	Ph	CH_3SO_2Na	75	118
O	Ph	$PhSO_2Na$	62	118
O	*p*-CH_3—C_6H_4	$PhNH_2$	<1	197
O	Ph	*o*-CH_3—C_6H_4—NH_2	40	197
O	*p*-CH_3—C_6H_4	*o*-CH_3—C_6H_4—NH_2	21	197
O	Ph	*p*-CH_3—C_6H_4—NH_2	47	197
O	*p*-$CH_3C_6H_4$	*p*-CH_3—C_6H_4—NH_2	25	197
O	Ph	*p*-OCH_3—C_6H_4—NH_2	50	197
O	*p*-CH_3—C_6H_4	*p*-OCH_3—C_6H_4—NH_2	52	197
O	Ph	*o*-OEt—C_6H_4—NH_2	70	197
O	*p*-CH_3—C_6H_4	*o*-OEt—C_6H_4—NH_2	59	197
O	Ph	*p*-OEt—C_6H_4—NH_2	40	197
O	*p*-CH_3—C_6H_4	*p*-OEt—C_6H_4—NH_2	47	197
O	Ph		54	197
O	*p*-CH_3—C_6H_4		32	197

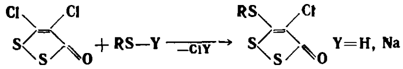
The difference in reactivity between substituents at positions 4 and 5 is attributed to the difference in polarity between the $C_{(4)}$ and $C_{(5)}$ carbon atoms (see above)[133]; great activity of the 5-halogen is indicated also by the vinylogy principle, since 5-chloro-1,2-dithiolen-3-one is a vinylogue of carboxylic acid chlorides[193].

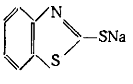
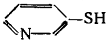
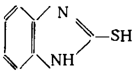
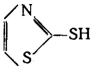
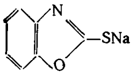
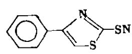
Table 20. 5-Alkylamino-4-chloro-1,2-dithiolens from 4,5-dichloro-1,2-dithiolens:



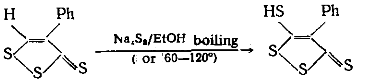
X	R	R'	Yield, %	Ref.	X	R	R'	Yield, %	Ref.
O	H	o-CH$_3$—C$_6$H$_4$	60	196	N—SO$_2$—C$_6$H$_5$	H	C$_6$H$_5$	57	193
O	H	m-CH$_3$—C$_6$H$_4$	85	196	N—SO$_2$C$_6$H$_4$CH$_3$-p	H	CH$_3$	36	193
O	H	p-CH$_3$—C$_6$H$_4$	85	196	ditto	H	n-C$_3$H$_7$	34	193
O	H	o-CH$_3$O—C$_6$H$_4$	77	196	ditto	H	n-C$_4$H$_9$	58	193
O	H	m-CH$_3$OC$_6$H$_4$	88	196	ditto	H	n-C$_{18}$H$_{37}$	58	193
O	H	p-CH$_3$O—C$_6$H$_4$	99	196	ditto	H	cyclo-C$_6$H$_{11}$	67	193
O	H	o-EtO—C$_6$H$_4$	69	196	ditto	H	HO(CH$_2$)$_3$	37	193
O	H	p-EtO—C$_6$H$_4$	98	196	ditto	H	H$_2$N(CH$_2$)$_2$	7.0	193
O	C$_2$H$_5$	C$_2$H$_5$	20	196	ditto	H	C$_6$H$_5$CH$_2$	64	193
O	H	Ph	94	196	ditto	H	C$_6$H$_5$	79	193
CH$_3$N	(CH$_2$)$_2$—O—(CH$_2$)$_2$		12	193	ditto	H	p-CH$_3$C$_6$H$_4$	61	193
NSO$_2$CH$_3$	(CH$_2$)$_2$—O—(CH$_2$)$_2$		87	193	ditto	H	o-OH—C$_6$H$_4$	34	193
NSO$_2$Ph	H	CH$_3$	44	193	ditto	CH$_3$	CH$_3$	53	193
ditto	H	n-C$_3$H$_7$	40	193	ditto	(CH$_2$)$_4$		80	193
ditto	H	n-C$_4$H$_9$	54	193	ditto	(CH$_2$)$_5$		77	193
ditto	H	n-C$_8$H$_{17}$	40	193	ditto	(CH$_2$)$_2$—O—(CH$_2$)$_2$		79	193
ditto	H	cyclo-C$_6$H$_{11}$	54	193	N—SO$_2$C$_6$H$_4$CH$_3$-p	H	C$_6$H$_5$NH	85	193
ditto	H	HO(CH$_2$)$_2$	33	193	N—CO$_2$Et	H	Ph	78	193
ditto	H	C$_6$H$_5$CH$_2$	44	193	N—CO$_2$Et	(CH$_2$)$_2$—O—(CH$_2$)$_2$		67	193
ditto	H	C$_6$H$_5$	72	193	NCOC$_6$H$_4$NO$_2$-o	H	p-CH$_3$C$_6$H$_4$	54	121
ditto	H	p-CH$_3$—C$_6$H$_4$	62	193	NCOC$_6$H$_4$NO$_2$-o	H	p-OEtC$_6$H$_4$	62	121
ditto	H	o-OH—C$_6$H$_4$	51	193	NCOC$_6$H$_4$NO$_2$-o	(CH$_2$)$_2$—O—(CH$_2$)$_2$		91	121
ditto	CH$_3$	CH$_3$	92	193	NCOC$_6$H$_3$(NO$_2$)$_2$-o, p	H	p-CH$_3$—C$_6$H$_4$	18	121
ditto	C$_2$H$_5$	C$_2$H$_5$	85	193	ditto	H	p-OCH$_3$—C$_6$H$_4$	24	121
ditto	CH$_3$	C$_6$H$_5$	35	193	ditto	H	p-OC$_2$H$_5$—C$_6$H$_4$	15	121
ditto	(CH$_2$)$_4$		76	193	ditto	(CH$_2$)$_4$		39	121
ditto	(CH$_2$)$_5$		73	193	ditto	(CH$_2$)$_2$—O—(CH$_2$)$_2$		56	121
ditto	(CH$_2$)$_2$—O—(CH$_2$)$_2$		87	193					

Table 21. Reaction of 4,5-dichloro-1,2-dithiolen-3-ones with thiols:

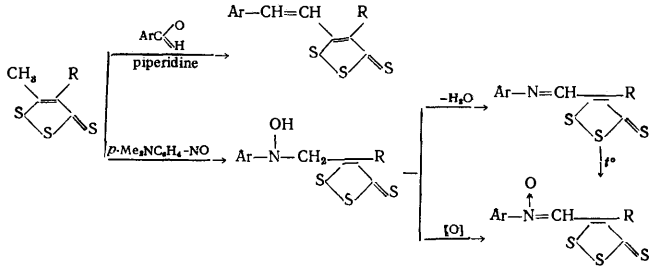


RSY	Yield, %	Ref.	RSY	Yield, %	Ref.
p-Cl-C$_6$H$_4$—SH	84	170, 195			
PhCH$_2$CH$_2$SH	93	195, 118			
EtO$_2$C—CH$_2$SH	75,5	195		76	120
MeO$_2$C—CH$_2$SH	53; 89	195, 118			
HO$_2$C—CH$_2$SH	32; 91	195, 118			
	97	195		88	120
CH$_3$SH	70	118			
EtSH	79	118			
HO(CH$_2$)$_2$SH	54	118			
iso-PrO$_2$C—CH$_2$—SH	58	118			
n-C$_{12}$H$_{25}$O$_2$C—CH$_2$—SH	52	118		71	120
C$_6$H$_5$SH	84	118			
p-CH$_3$C$_6$H$_4$SH	78	118			
p-NO$_2$C$_6$H$_4$SH	89	120			
C$_6$H$_5$CH$_2$SH	89	120			
o-Cl-C$_6$H$_4$CH$_2$SH	70	120			
C$_6$H$_5$CH(CH$_3$)$_2$SH	94	120			
	82	120		63	120

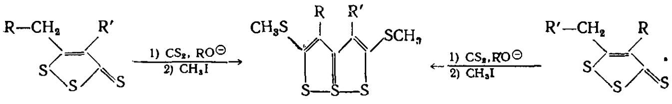
An unusual reaction has been reported[199] between sodium disulphide and 4-phenyltrithione, when 5-mercaptotrithione is obtained:



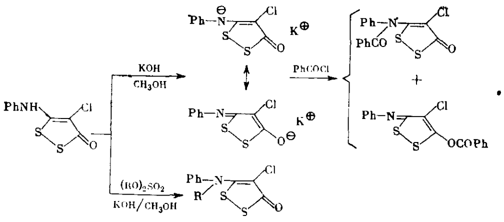
Trithiones containing a methyl or substituted methyl group at position 5 react with aromatic aldehydes to form aldol condensation products; an anil and a nitrone are obtained with p-nitroso-NN-dimethylaniline[10,81,101]:



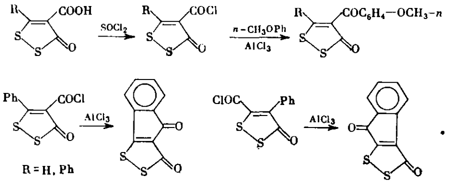
The condensation with carbon disulphide of trithiones containing a substituted methyl group at position 5, in the presence[178] or the absence[200] of a base, gives after methylation bismethylthiothiothiophthens:



A 5-amino-group present in a 1,2-dithiolen-3-one may be both acylated and alkylated[196,201]:

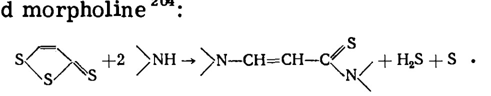


The stability of the 1,2-dithiolen ring is demonstrated by Friedel–Crafts reactions[82,202,203]:

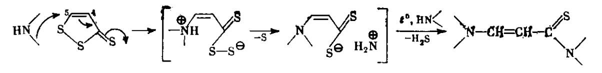


(*f*) Reactions with nucleophilic reagents accompanied by ring fission

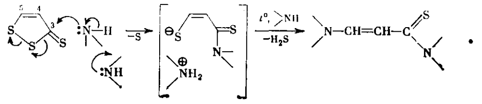
The action of nucleophiles on reactive 1,2-dithiolen-3-thiones opens the ring. Thus β-aminothioacrylamides are formed from unsubstituted trithione and its 4-cyano-derivative with excess of such amines as aniline, *p*-toluidine, and morpholine[204]:



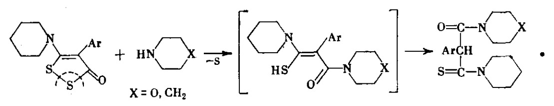
However, the authors' assumption of initial rupture of the $C_{(5)}-S_{(1)}$ bond



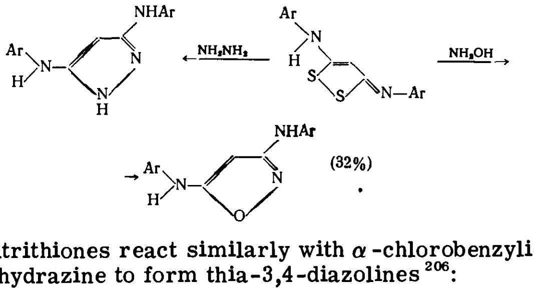
appears questionable. A more probable mechanism involves synchronous cleavage of C(S)–S and S–S bonds, with the amine attacking not $C_{(5)}$ but the thiocarbonyl $C_{(3)}$ atom:



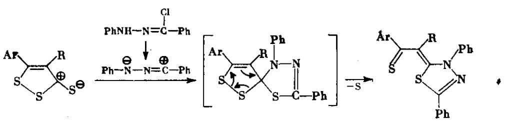
The proposed mechanism is consistent with the cleavage of 4-aryl-5-piperidino-1,2-dithiolen-3-ones by morpholine and piperidine, when diamides of arylmonothiomalonic acids are formed[197]:



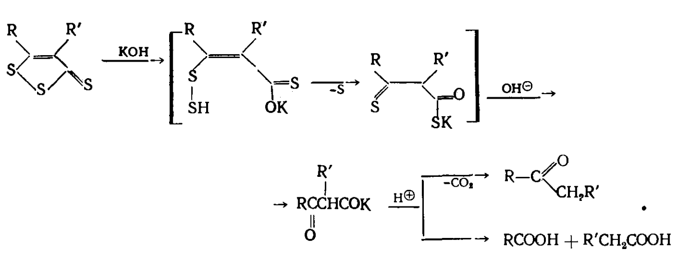
The reactions of 5-arylamino-1,2-dithiolen-3-imines with hydrazine (or phenylhydrazine) and with hydroxylamine involve ring opening with formation of a pyrazole and a 1,2-oxazole[191,205]:



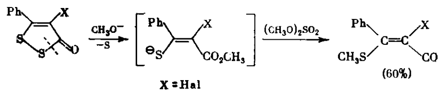
5-Aryltrithiones react similarly with α-chlorobenzylidene-phenylhydrazine to form thia-3,4-diazolines[206]:



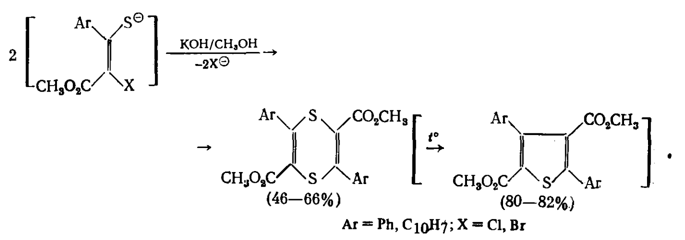
The 1,2-dithiolen ring is cleaved by alkalis[207] still more easily than by amines. Hydrolysis of trithiones with excess of alkali yields derivatives of acetoacetic acid, which then split into a ketone or the corresponding acids[10,101]:



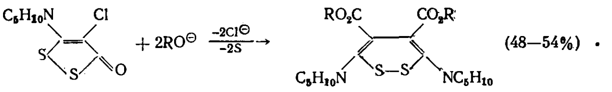
The hydrolysis of 5-phenyl-1,2-dithiolen-3-one by excess of potassium hydroxide gives acetophenone[71]. However, the action of an equimolecular quantity of methanolic alkali yields the β-methylthio-cinnamic ester[208]:



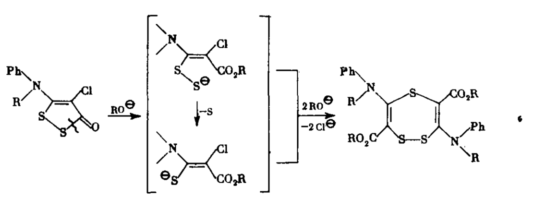
In the alkaline cleavage of 5-aryl-4-halogeno-1,2-dithiolen-3-ones the resulting fragments undergo "head to tail" condensation to 1,4-dithiacyclohexadiene derivatives with liberation of halide ions[120,207]:



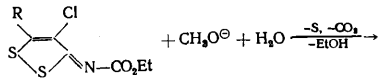
When 4-chloro-5-piperidino-1,2-dithiolen-3-ones are hydrolysed, such fragments undergo "head to head" dimerisation with formation of 1,2-dithiacyclohexadiene derivatives[208,209]:

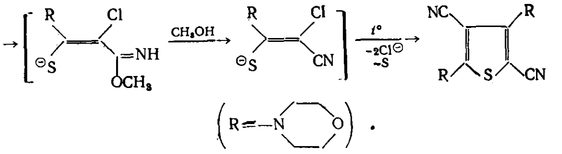


In the reaction of 5-*N*-alkylanilino-4-chloro-1,2-dithiolen-3-ones with alcoholic alkali the primary product of cleavage of the cyclic S–CO bond is preserved in only one unit of the resulting 1,2,5-trithiacycloheptadiene structure[194,210]:

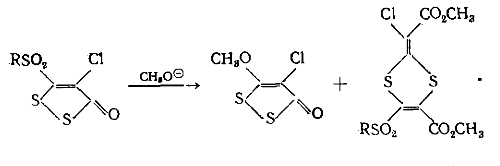


4-Chloro-1,2-dithiolen-3-imines are far more stable and are broken down only by boiling methanolic alkali, with the formation of thiophen derivatives[193]:

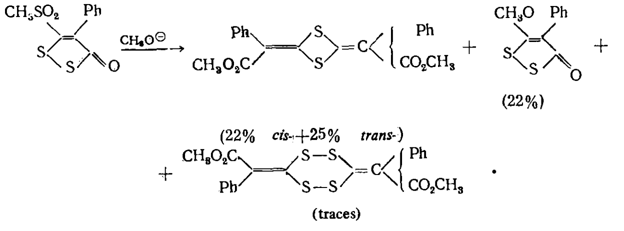




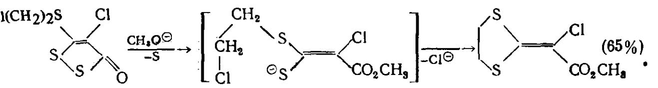
The reaction of 4-chloro-5-sulphonyl-1,2-dithiolen-3-ones with alkoxides gives 1,3-dithiafulvalenes together with the 5-alkoxy-4-chloro-1,2-dithiolen-3-one:[211]



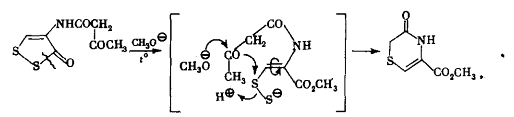
In the absence of a 4-chloro-substituent competing reactions lead to the formation of several compounds, with 2,4-dialkylidene-1,3-dithietans predominating[211]:



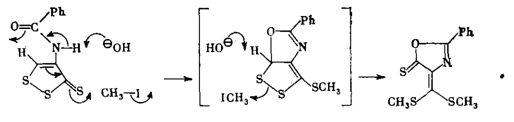
The alkaline cleavage of 4-chloro-5,2′-chloroethylthio-1,2-dithiolen-3-one yields a 2-alkylidene-1,3-dithiolan[211]:



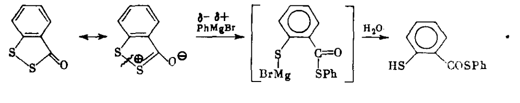
Under these conditions 4-acylamino-1,2-dithiolen-3-ones form nitrogen heterocycles. Thus the 4-acetoacetamido-derivative gives a low yield of a 3-oxodihydrothiazine derivative[212]:



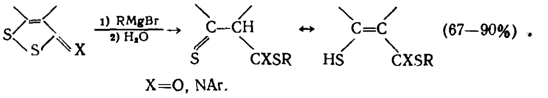
However, methylation of 4-acylamino-trithiones in the presence of potassium t-butoxide or hydroxide gives oxazoline-5-thiones[213]:



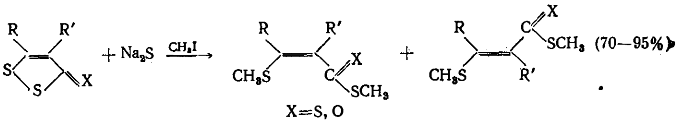
4,5-Benzo-1,2-dithiolen-3-one is cleaved by phenylmagnesium bromide at the disulphide bond with the formation of *o*-mercaptothiobenzoic *S*-esters[214]:



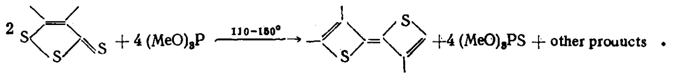
5-Amino-1,2-dithiolen-3-ones and the 5-aryl-3-imines react similarly with Grignard reagents, but the cleavage products exist predominantly in the thioketone—not the thioenolic—form[215,216]:



The reaction of trithiones and 1,2-dithiolen-3-ones with sodium sulphide also involves rupture of the disulphide bond with formation of unsaturated mono- or di-thioesters[217]:



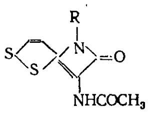
Heating alkylated trithiones with excess of an organic phosphorus(III) compound is assumed to yield a thietenylidene[218]:



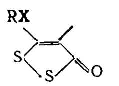
4. Applications

(*a*) Medicinals

Trithiones occur in Nature (in plants)[95]. The 1,2-dithiolen ring forms a fragment of the antibiotics thiolutin (VIa), holomycin (VIb), etc.[212] Several thiones are used in medicine to stimulate the functioning of the liver and the gall-bladder[95]. 5-*p*-Methoxyphenyl-1,2-dithiolen-thione—Sulfarlem (DDR)[219]—and -3-one[220] are non-toxic bile-producing preparations, but the 4-aryltrithiones are less effective[219]. Trithiones, especially those containing a thiophen residue at position 5, have a diuretic effect[221].



(VI); R=CH_3 (a), H(b)



(VII); X=SO_2 (a), SO(b), S(c)

(*b*) Insecticides

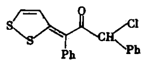
4-Aroyl-5-aryltrithiones[85], 5-chloro-4-phenyl-1,2-dithiolen-3-ones[222], and *N*-aryl-4,5-dichloro-1,2-dithiolen-3-imines[223] are fungicides suitable for the treatment of grain. 1,2-Benzodithiolen-3-thiones and -oximes both possess antifungal properties[189,190,224]. 5-Alkyl-sulphonyl-, -sulphinyl, and -thio-1,2-dithiolen-3-ones (VIIa–c)[170,195,225–227] are bactericides and fungicides effective against moulds and pathogenic fungi[170,195], as are also 5-aminated 4-chloro-1,2-dithiolen-3-ones[225,226] and -3-phenyl-imines[119]. 5-Methoxycarbonylthio- and 5-morpholinothio-4-phenyltrithiones are used as insecticides and fungicides[228,229].

(*c*) Additives to lubricating oils

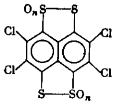
Alkylated trithiones can be used in lubricating oils as antioxidant and anti-seizing additives. 4-Neopentyl-5-t-butyltrithione is especially effective because of its better solubility in petroleum oils[230]. Trithione *S*-oxides[168,169] and products of the reaction of trithiones with polyamines[231] and phosphites[218] are multipurpose additives for lubricating oils. 4-Substituted trithiones act as corrosion inhibitors in lubricating oils[93].

(*d*) Other fields

Chlorinated 3-acylmethylene-1,2-dithiolens (VIII),[126] chlorinated naphthodithioles (IXa), and dioxides of the latter (IXb)[99]



(VIII)



(IX); *n* = 0 (a), 2 (b)

are used as yellow colorants for thermoplastics. Compounds (IX) are employed also as semiconductors and dielectrics[99]. 5-Methoxycarbonylthio- and 5-morpholinothio-4-phenyltrithiones find application as vulcanisation accelerators[228,229].

Phenylated trithiones are used in analytical practice for the extraction and the photometric or gravimetric determination of platinum(II) or mercury(II) as water-insoluble orange complexes $M^{II}Cl_2R_2$.[103,232,233]

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The Concept of Vacant *d* Orbitals and the Causes of the Differences between the Properties of Nitrogen and Phosphorus Compounds

D.A.Bochvar, N.P.Gambaryan, and L.M.Epshtein

Comparison of non-empirical calculations on analogous nitrogen and phosphorus compounds shows that the presence of vacant *d* orbitals in the valence shells of the elements in the Third Period cannot be the real cause of the differences between the properties of nitrogen and phosphorus compounds and that the effects are ultimately determined by the differences between the effective sizes of the valence *s* and *p* orbitals of these elements.
The bibliography includes 47 references

CONTENTS

I. INTRODUCTION

This review discusses the problem which properties of nitrogen and phosphorus atoms determine the fundamental differences between the properties of the compounds of these elements. It begins with a brief account of the properties of isolated nitrogen and phosphorus atoms and their valence states. The discussion is based on the standpoint necessary for developing the subsequent reasoning.

II. NITROGEN AND PHOSPHORUS ATOMS AND THEIR VALENCE STATES

The properties of nitrogen and phosphorus atoms are determined by their positions in Mendeleev's periodic table. The structure of the Table became comprehensible after quantum mechanics had been developed and had yielded the solution of the problem of the hydrogen atom. It was found that the electron in the hydrogen atom can have a discrete (and not continuous as in the classical treatment) series of states whose energy E_n is determined by the principal quantum number n:

$$E_n = -\frac{me^4}{2\hbar^2}\cdot\frac{1}{n^2};\quad n = 1, 2, 3 \ldots .$$

In addition to the energy, the state of the electron is characterised by its angular momentum, which is determined by the orbital quantum number l:

$$M^2 = \hbar^2 l(l+1);\quad l = 0, 1, 2 \ldots$$

The range of momenta in states with a definite energy is limited:

$$l \leqslant n-1.$$

States with zero angular momentum ($l = 0$) are referred to as *s* states, those corresponding to $l = 1$ are *p* states, those corresponding to $l = 2$ are *d* states, etc. When the *s* states, for which the angular momentum is zero, are excluded, the states are distinguished by the direction of the angular momentum, which is determined by the magnetic quantum number m:

$$M_z = \hbar m;\quad m = 0, \pm 1, \pm 2, \ldots, \pm l.$$

Fig. 1 presents a schematic arrangement of the possible states of the electron in the hydrogen atom. The excited levels of hydrogen are degenerate, i.e. a whole set of different states corresponds to the same energy. The energy levels are degenerate not only as regards direction but also as regards momentum, i.e. the energies of the *s*, *p*, and *d* states are identical.

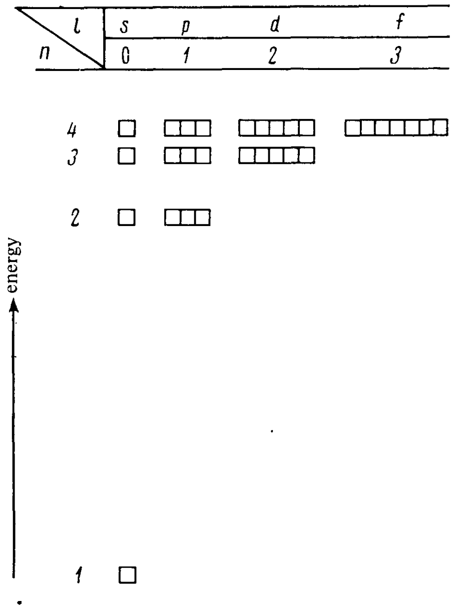


Figure 1. Schematic illustration of the possible electronic states in the hydrogen atom.

If the electrons did not interact, an identical pattern of possible electronic states would persist in a multielectron atom and it would be possible to determine the structure of any atom by filling these states in succession, taking into account the Pauli principle. In reality electrons repel one another. For example, the 2*s* electron of lithium is not only not attracted to the nucleus, but is actually repelled by the inner 1*s* electrons (Fig. 2), the overall effects of which can be described as shielding of the nucleus—the decrease of the actual nuclear charge to an "effective" charge. The shielding conditions depend on the nature of the electron cloud. The density of the electron cloud in the *s* states is a maximum in the region of the nucleus; this applies not only to the 1*s* state but also to the 2*s* and 3*s* states (Fig. 3*a*). In the *p* states, the density of the electron cloud at the nucleus is zero (Fig. 3*b*) and in the *d* states the density is again zero at the nucleus and increases very slowly (Fig. 3*c*). Accordingly, the shielding of the nucleus by other electrons is much more marked for a *d* electron than for a *p* electron and for the latter it is more marked than for an *s* electron. As a result, the degeneracy as regards momentum is removed: the energies of the *s*, *p*, and *d* electrons are no longer the same. Fig. 4 presents a schematic arrangement of the possible electronic states in a multielectron atom.

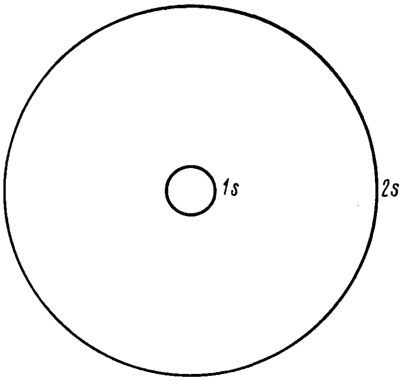


Figure 2. The lithium atom. The radii of the circumferences correspond to the maximum radial densities of the 1*s* and 2*s* electrons[1].

Nitrogen and phosphorus atoms are located in Group V but in the Second and Third Periods. We shall consider how their properties are determined by their positions. We shall begin with the ionisation potential—a property of decisive importance for chemistry (Fig. 5).

Fig. 2 shows that the valence electron of lithium is remote from the nucleus from which it is effectively shielded by the 1*s* electrons and the ionisation potential is therefore very low. In the beryllium atom, the increased nuclear charge is incompletely shielded, and the ionisation potential is greater. Although the nuclear charge has again increased in the boron atom, the additional electron is now located in a *p* orbital for which the shielding is more marked, as a result of which the ionisation potential is smaller than for beryllium. The additional electron in carbon is located in the next vacant *p* orbital and the increased nuclear charge, which is incompletely compensated by shielding, leads to an increase of the ionisation potential; this effect is even greater for nitrogen and in the oxygen atom the additional electron enters a *p* orbital already occupied by an electron. The mutual repulsion of the two electrons in the same orbital is so powerful, that, despite the increased nuclear charge, the ionisation potential of oxygen is smaller than that of nitrogen. Thus the ionisation potential of nitrogen is greater than those of its immediate neighbours—not only carbon but also oxygen:

	C	N	O
I, eV	11.256	14.53	13.614

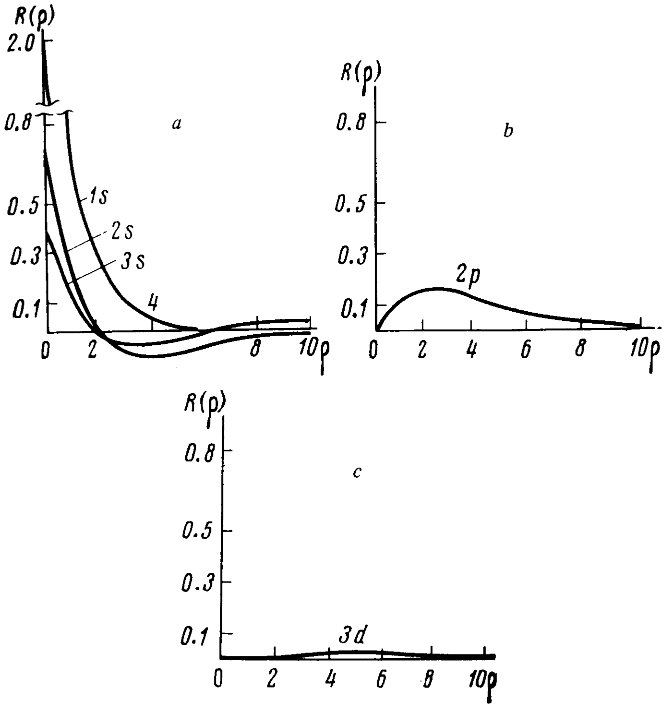


Figure 3. The radial wave functions *R*(ρ) of the hydrogen atom (ρ is the distance from the nucleus in atomic units).

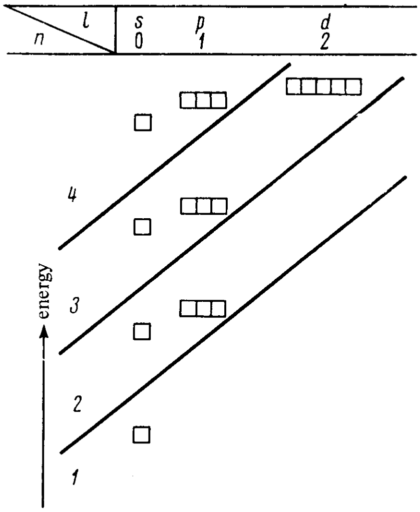


Figure 4. Schematic illustration of the arrangement of atomic orbitals in terms of energies in a multielectron atom.

The same qualitative pattern holds for the Third Period: the ionisation potential of phosphorus is greater than those of silicon and sulphur:

	Si	P	S
I, eV	8.15	10.48	10.36

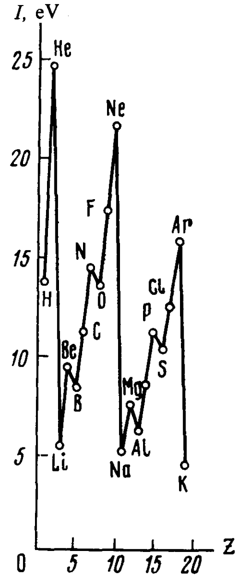


Figure 5. Ionisation potentials of atoms.

However, despite the complete repetition of qualitative features, there is a considerable quantitative difference between nitrogen and phosphorus. The valence electrons of the phosphorus atom are at a much greater distance from the nucleus than in nitrogen, so that, despite the higher effective nuclear charge, the ionisation potential of phosphorus is approximately 4 eV smaller than that of nitrogen.

Another atomic property very important for chemistry is electron affinity. In the carbon atom, the nucleus is incompletely shielded by valence electrons, there is a vacant *p* orbital, and the atom exhibits an appreciable electron affinity. In the nitrogen atom, the additional electron must enter a *p* orbital which is already occupied and the interelectronic repulsion is so great that the electron affinity is negligible. In the oxygen atom, the increased nuclear charge partly compensates this effect and the electron affinity increases:

	C	N	O
E, eV	2.1	0.05	1.47

The same qualitative pattern is repeated for the atoms of the Third Period: the electron affinity of phosphorus is smaller than that of its neighbours—silicon and sulphur:

	Si	P	S
E, eV	1.46	0.77	2.07

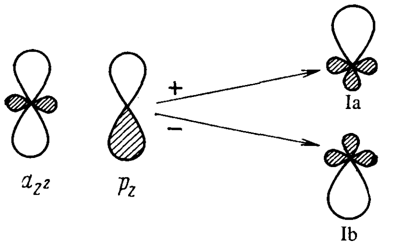
On the other hand, the mutual repulsion of the electrons located in the same orbital in the phosphorus atom with its larger valence orbitals is less marked than in nitrogen. As a result, the electron affinity of phosphorus is greater than that of nitrogen. The more ready deformation of the electron cloud of phosphorus under the influence of external fields, i.e. the greater polarisability of the phosphorus atom compared with the nitrogen atom, is associated with the greater size of the valence orbitals of the phosphorus atom and the greater diffuseness of its electron cloud. Consequently, owing to the greater size of phosphorus orbitals compared with nitrogen orbitals, the ionisation potential of phosphorus is much smaller, its electron affinity is much greater, and its polarisability is greater.

We shall consider yet another difference between phosphorus and nitrogen. The valence shell of the phosphorus atom contains *d* orbitals and the question of their properties arises. The states of hydrogen are arranged in Fig. 1 in terms of energies on a uniform scale. A similar arrangement of the electrons in phosphorus is impossible (the ionisation potential of the valence electron of the phosphorus atom is of the order of 10 eV, while the ionisation potential of the 1*s* electrons of phosphorus is of the order of thousands of electron-volts). Fig. 4 merely shows qualitatively that the energy of the vacant *d* orbitals is higher than that of the *s* and *p* orbitals of the next shell. It is seen from the atomic spectra of phosphorus[2] that the first transitions are $3p \rightarrow 4s$ (7–8 eV), are followed next by $3p \rightarrow 4p$ transitions (8–8.5 eV), and only then by transitions to 3*d* orbitals (about 9 eV). Consequently, despite the fact that the *d* orbitals of the phosphorus atom are located in the valence shell, they are less favourable than the 4*s* and 4*p* orbitals in the next shell. As already mentioned, this is because the shielding of the *d* orbitals from the nucleus by other electrons is particularly effective. The weak attraction of *d* electrons to the nucleus leads to the expansion of their orbitals. As a result of the diffuseness of the *d* orbitals of phosphorus, their overlapping with the valence orbitals of neighbouring atoms is negligible. With this statement, we complete the consideration of the properties of isolated phosphorus and nitrogen atoms and proceed now to an examination of their valence states.

Phosphorus and nitrogen atoms each have three unpaired electrons located in *p* orbitals. The p^3 state may be regarded as their ground valence state, despite the fact that the bonding orbitals acquire some *s* character and the lone electron pair occupies an orbital with an admixture of *p* character and not a pure *s* orbital[3].

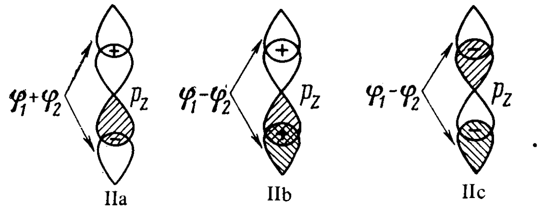
The lone electron pair can form a bond with a proton, with an alkyl cation, with BF_3, and in general with Lewis acids. This results in the formation of ammonium and phosphonium compounds in which tetravalent nitrogen and phosphorus cations are in a tetrahedral sp^3-hybrid valence state. If the substituents are not the same, the tetrahedron is distorted, the distortion being particularly pronounced in compounds such as phosphine and amine oxides; nevertheless, the valence states in these compounds can be regarded as largely sp^3 states. Compounds of the type NR_5 are known, but their discoverer (Schlenck) already showed that the bonds in such compounds are non-equivalent[4]. They are salt-like and contain the tetravalent ammonium cation NR_4^+ and the carbanion R^-.

On the other hand, penta- and hexa-coordinate compounds with more or less equivalent bonds are known for phosphorus. Pentacoordinate phosphorus compounds, for example PF_5, have a trigonal bipyramidal structure. It has come to be assumed that the valence shell of phosphorus is expanded in these compounds owing to the vacant *d* orbital. Bonds with three equatorial ligands are formed by the trigonal sp^2-hybrid phosphorus orbitals, while the remaining p_Z orbital is hybridised with the d_{Z^2} orbital in order to form bonds with the axial ligands. The hybrid *dp* orbital (Ia) obtained when the above orbitals are combined is involved in the formation of a bond with the upper ligand and the residual hybrid *dp* orbital (Ib) forms a bond with the ligand located at the lower vertex of the bipyramid.



It is therefore usually assumed[5] that phosphorus exists in the dsp^3 valence state.

Nevertheless the involvement of *d* orbitals is by no means necessary for the description of the bonding in pentacoordinate phosphorus compounds. This is easily shown using the molecular orbital method[6]†. The linkages with the three ligands in the equatorial plane are again regarded as two-centre bonds formed by the trigonal sp^2-hybrid orbitals of phosphorus. In order to describe the bonds with the axial ligands, we construct molecular orbitals from the p_Z orbital of phosphorus and the atomic orbitals of the ligands. The overlap integral for the symmetrical combination of the ligand orbitals $\varphi_1 + \varphi_2$ with the p_Z orbital of phosphorus is zero‡ [the positive overlap with the upper lobe of the p_Z orbital is compensated by the negative overlap with the lower lobe of this orbital (IIa)]. The interaction is therefore impossible and this combination constitutes the non-bonding orbital ψ_2, the energy of which is equal to the energy of the atomic orbitals of the ligands (Fig. 6).



On the other hand, the antisymmetric combination of the ligand orbitals $\varphi_1 - \varphi_2$ forms with the p_Z orbital of phosphorus the energetically extremely favourable and highly bonding three-centre molecular orbital ψ_1 (Fig. 6) [the positive overlap of the ligand orbitals with the upper lobe of the p_Z orbital of the phosphorus atom $\oplus\cdot\oplus$ is supplemented by the positive $\ominus\cdot\ominus$ overlap with the lower lobe (IIb)] and the three-centre antibonding molecular orbital ψ_3 [the negative overlap $\oplus\cdot\ominus$ with the upper lobe of the p_Z orbital is added to the negative $\ominus\cdot\oplus$ overlap with the lower lobe (IIc)].

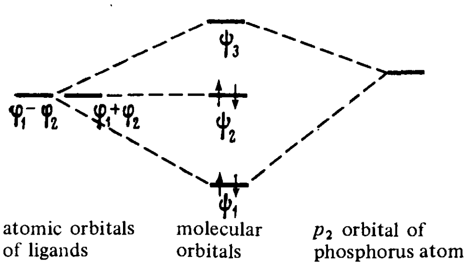


Figure 6. Correlation diagram for a three-centre bond.

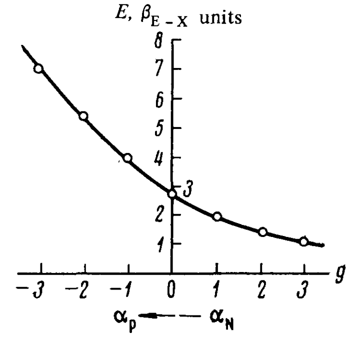


Figure 7. Dependence of the energy E of the three-centre bond X–E–X on the Coulombic integral of the central atom $\alpha_E = \alpha_X + g\beta(E - X)$ (the Hückel approximation). The arrows show the direction of the change in α_E from N to P in parallel with the change in the ionisation potential.

In the resulting molecular orbitals—the bonding orbital ψ_1, the non-bonding orbital ψ_2, and the antibonding orbital ψ_3—four-electrons should be located: the two electrons of the lone pair of phosphorus and one electron from each ligand. They occupy the bonding ψ_1 molecular orbital and the non-bonding ψ_2 orbital and, although the electrons in the non-bonding orbital give no energy gain, the bonding molecular orbital is energetically so favourable that the two electrons located in it are sufficient to ensure the formation of a linkage between the phosphorus atom and the ligands located at the upper and lower vertices of the bipyramid. The energy of the three-centre "four-electron" bond depends strongly on the energy of the lone pair electrons. This energy increases rapidly with decrease of the ionisation potential of the lone electron pair and the three-centre bond must therefore be much more favourable for phosphorus than for nitrogen (Fig. 7).

We shall consider now how the above description is altered when account is taken of the *d* orbital of the phosphorus atom. In contrast to the p_Z orbital, the *d* orbital

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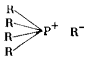
† The description by the valence bond (VB) method without resorting to *d* orbitals corresponds to the resonance of five ionic structures:



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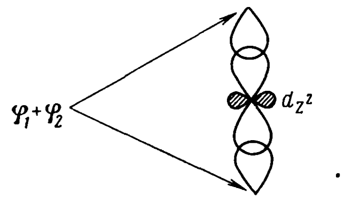
‡ The overlapping of the functions is described by the integral of the product of these functions (the overlap integral S): $S = \int \bar{\Phi}_1 \Phi_2 d\tau$ (integration over the entire space). The parts of the space where the two overlapping functions have the same sign make a positive contribution to the integral, while those regions where the signs of the functions are different make a negative contribution.

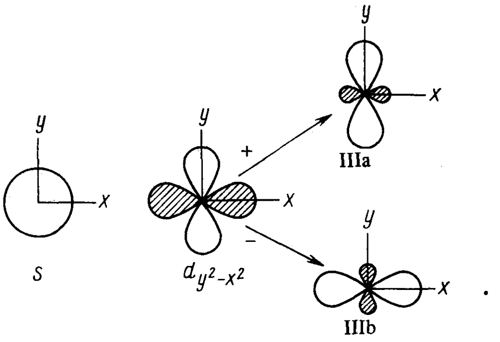
of phosphorus can interact with the symmetrical combination $\varphi_1 + \varphi_2$ of the ligand orbitals (IId):



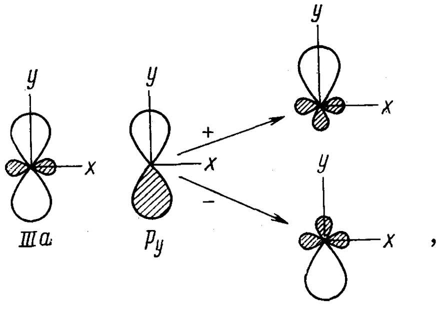
IId

But, since the d orbital is energetically unfavourable and very diffuse, its interaction can only be very weak. Because of it, the non-bonding molecular orbital ψ_2 becomes slightly bonding. However, this weak interaction does not play a fundamental role.

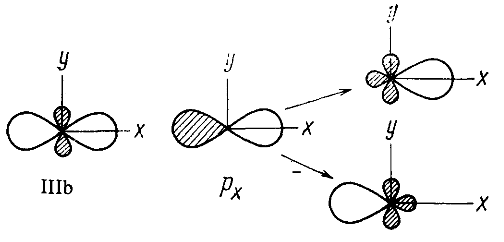
In the traditional description of ions containing hexacoordinate phosphorus such as PF_6^-, one postulates an expansion of the valence shell of phosphorus by two d orbitals. One of these, the d_{z^2} orbital, is hybridised with the p_z orbital, forming hybrid dp orbitals directed to the upper and lower ligands. This description is exactly the same as that of the bonds with the axial ligands in PF_5. A second d orbital of phosphorus, namely the $d_{y^2-x^2}$ orbital, is invoked, in addition to the s, p_x, and p_y orbitals to describe the bonds with the four ligands in the equatorial plane. We shall describe the hybridisation in stages. On combining the $d_{y^2-x^2}$ orbital with the s orbital, we obtain orbitals extended along the y axis, ($s + d_{y^2-x^2}$, IIIa) and along the x axis ($s - d_{y^2-x^2}$, IIIb):



The first of these forms with the p_y orbital two orbitals directed to the ligands located on the y axis:



while the second forms with the p_x orbital two orbitals directed to the ligands located on the x axis:



Each of the six hybrid phosphorus orbitals obtained forms a two-centre bond with the atomic orbitals of the ligands. In this description, it is assumed that phosphorus is in the d^2sp^3 valence state.

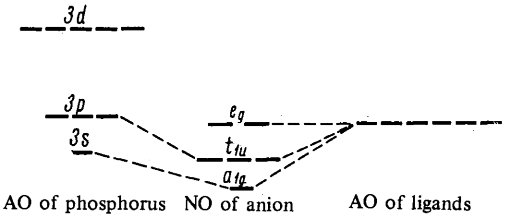


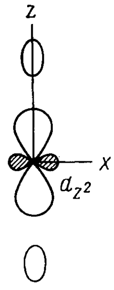
Figure 8. Correlation diagram for an octahedral anion.

However, as for the pentacoordinate phosphorus compounds, it is found that the hypothesis of the expansion of the valence shell is not essential for a description of the bonds between phosphorus and the ligands in its hexacoordinate compounds. Indeed, the sum of the atomic orbitals of all the ligands is combined with the s orbital of phosphorus, forming an energetically very favourable bonding seven-centre molecular orbital (group designation a_{1g}, Fig. 8).

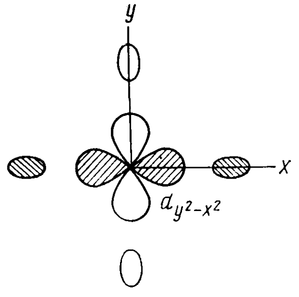
The antisymmetric combination of the ligand orbitals located on the z axis forms a strongly bonding three-centre molecular orbital with the p_z orbital of the phosphorus atom [similar to the three-centre linkage (IIb) between phosphorus and the axial ligands in PF_5]. Exactly the same three-centre molecular orbitals are obtained from the p_x (and p_y) orbitals of the phosphorus atom and the antisymmetric combination of the orbitals of the ligands located along the x (and y) axis. The energies of these three three-centre molecular orbitals are the same, i.e. they are degenerate (group designation t_{1u}, Fig. 8).

Eight electrons are located in the resulting orbitals—one seven-centre and three three-centre orbitals. The remaining four electrons (there are altogether twelve electrons: six from the ligands, five from the phosphorus atom, and one additional electron, since hexacoordinate phosphorus species exist in the form of anions) are distributed in two degenerate non-bonding molecular orbitals formed from the ligand orbitals alone (group designation e_g, Fig. 8). These two non-bonding molecular orbitals are shown in diagrams IVa and IVb. Although the last four electrons make no contribution to the bonding, the energy gain due to the eight electrons located in the strongly bonding molecular orbitals is so great that it is quite sufficient to account for the bonding between phosphorus and the ligands in its octahedral anions (Fig. 8).

We shall now consider the changes in the above pattern when account is taken of the phosphorus *d* orbitals. The symmetry of two of the phosphorus *d* orbitals (the d_{z^2} and $d_{y^2-x^2}$ orbitals) is such that they can interact with the non-bonding molecular orbitals e_g.



(IVa)



(IVb)

Next one can repeat what has already been said in the discussion of the pentacoordinate phosphorus compounds. Owing to the diffuseness and the energetically unfavourable nature of the phosphorus *d* orbitals, this interaction makes no significant contribution to the bonding: the non-bonding orbitals e_g become slightly bonding. It is clear from the foregoing that the concept of the expansion of the valence shell of phosphorus and of the existence of its dsp^3 and d^2sp^3 valence states is not essential for the description of the bonding in its pentacoordinate and hexacoordinate compounds.

III. NON-EMPIRICAL CALCULATIONS ON ANALOGOUS NITROGEN AND PHOSPHORUS COMPOUNDS

We shall now proceed to a comparison of the main classes of nitrogen and phosphorus compounds and shall attempt to find a fairly probable physical explanation of the differences between their properties. The traditional explanation of these properties is based on the concept of *d* orbitals. The concept of vacant *d* orbitals of silicon, phosphorus, and sulphur is widely used in the discussion of the properties of the compounds formed by these atoms[7-9]; *d* orbitals are invoked to account for the characteristics of the elements of the Third Period in relation to those of the Second Period.

The concept of *d* orbitals is based on the fact that the valence electrons of the elements of the Second Period are in the second shell, where there are no *d* orbitals, while the valence electrons of the elements in the Third Period are in the third shell. Apart from the *s* and *p* states, *d* states are possible in the third shell. Consequently, in contrast to the elements of the Second Period, those of the Third Period have vacant *d* orbitals in the valence shell. This led to the conclusion that the valence shell may be expanded and that additional bonds may be formed in pentacoordinate and hexacoordinate compounds via the *d* orbitals. The electron-accepting properties of the elements of the Third Period are accounted for by these orbitals and bonding with these elements and reactivity have been described with their aid, for example, by Ivanov and Zheltukhin[10]. This concept proved attractive and has been rapidly and extensively adopted[11]. This is, as it were, the chemical aspect of the problem of vacant *d* orbitals.

Qualitative considerations were followed by attempts to confirm them by calculations, which immediately encountered difficulties[12,13]. It was shown above that the *d* orbitals of the phosphorus atom are energetically very unfavourable and diffuse and are therefore incapable of effective interaction. This is also true of the *d* orbitals of the silicon and particularly sulphur atoms[2]. When atomic *d* orbitals are used in the calculation, as has been done for other valence orbitals, it is therefore immediately found that the *d* orbitals can play no role. It was then postulated that the atomic *d* orbitals in the molecule are altered (compressed), and modified *d* orbitals began to be used in calculations in place of the *d* orbitals of the free atoms. Since the contribution of these modified orbitals is found to be appreciable (see, for example, Refs. 14–17), it was concluded on this basis that the calculation confirms the *d* orbital concept.

Nevertheless the modified *d* orbitals have essentially no relevance to the vacant orbitals in the valence shell of the atom. They play the role of corrections in the calculation[18]. Thus a new aspect of the problem of *d* orbitals arose. In recent years there has been a vigorous growth of the number of quantum-chemical calculations, increasingly complex computational methods being devised and applied. For each new version of the calculation, the methodological problems have been solved, particularly the problem of the basis set—the set of initial functions from which the wave function of the molecule is constructed. The specific problem of the advantages of expansion of the basis set by additional functions of the *s* and *p* type or functions of the *d* type has been solved among others. This problem is associated with purely methodological difficulties and its chemical significance is almost or completely nil. The inadequate separation of these two aspects of the *d* orbital problem entails a multiplicity of misunderstandings. In the discussion of the concept of *d* orbitals, it is therefore useful to enumerate the possible situations in order to examine the available data and to attempt to discover which situation corresponds to reality.

1. Vacant atomic *d* orbitals of the valence shell of the elements of the Third Period influence directly the chemical properties of the latter, interacting effectively with the valence orbitals of the neighbouring atoms.

2. Orbitals of the *d* type have nothing in common with the atomic orbitals. They are introduced into the calculations in order to expand the basis set and play the role of corrections. Such corrections, which are in no way related to the presence or absence of *d* orbitals in the valence shell, can be introduced also into calculations on compounds of the elements of the Second Period. It may then be found that (a) the role of the *d*-type corrections in calculations on compounds of the elements of the Second and Third Periods is approximately the same or (b) the role of *d*-type corrections in calculations on compounds of the elements of the Third Period is much greater than in calculations on compounds of elements of the Second Period.

The considerations adduced in Section II are sufficient to rule out the first possibility. Orbitals whose energy exceeds that of the valence orbitals approximately by 10 eV (this is in fact the energy of the vacant *d* orbitals of the phosphorus atom) cannot have an appreciable influence on chemical properties and cannot effectively interact with the valence orbitals of the neighbouring atoms. The chemistry of the elements of the Third Period also provides evidence against the first possibility. However great the differences between the chemical properties of the elements of the Third and Second Periods, they are in no way comparable to the truly radical changes which occur in the presence of "working" vacant orbitals. Indeed, the appearance of such *d* orbitals alters the initial form of Mendeleev's periodic table and leads to the appearance of a class of completely unusual elements—the transition metals [$(n-1)$ *d* orbitals]. The presence of "working" vacant orbitals in the second shell is responsible for the tervalence of boron and the quadrivalence of carbon, which determine the entire chemistry of these elements (*p* orbitals). The existence of five chemically significant vacant *d* orbitals should have converted phosphorus into an electron-deficient element, which is not the case. The differences between the properties of phosphorus and nitrogen are large, but, as we shall see below, can be fully accounted for by the differences between the properties of the *s* and *p* valence orbitals of these elements.

However, having recognised that the role of *d* orbitals reduces to that of computational corrections, one must nevertheless elucidate the comparative importance of these corrections in calculations on compounds of the elements of the Third and Second Periods[19]. It is quite likely that the *d*-type corrections for elements of the Third Period are much greater than for elements of the Second Period, since the electronic systems of the former are much more complex and their orbitals are larger and more diffuse. If the *d*-orbital type corrections were indeed larger for the elements of the Third Period, they might assume a new importance. Without being in any way a true physical cause of the differences between the properties of the elements of the Third and Second Periods, the *d* orbitals might be used as a convenient language for the description of these differences. The widespread occurrence of the *d*-orbital "explanations" in the chemical literature might then be in a sense justified (with the essential proviso that the language be used correctly). Clearly, in view of the approximately identical values of the *d*-orbital corrections in calculations on compounds of elements of the Third and Second Periods (situation 2*a*), *d* orbitals can be used neither for the explanation nor for the description of the differences between the properties of these compounds. Thus the special role of *d* orbitals in phosphorus might be considered only if it were found that the *d*-orbital corrections for the phosphorus atom are much greater than for the nitrogen atom. Since this formulation of the problem is as yet not altogether usual, the comparison will have to be made largely on the basis of studies of different workers carried out at different times for quite different purposes.

We shall begin the comparison with elemental phosphorus and nitrogen. In 1967 Boyd and Lipscomb[20] carried out a calculation on the P_2 molecule and reached the following conclusion: "This study establishes a quantitative evaluation of the large participation of 3*d* orbitals in molecular bonding of P, and hence qualitatively of second-row atoms.... The total energies ... are significantly improved, and the electron densities are significantly changed upon the inclusion of 3*d* orbitals". Indeed the application of *d*-orbital corrections led to an energy gain of 3.75 eV. However, in their conclusion the authors failed to take into account the studies of Nesbet[21], who introduced orbitals of the *d* type into a calculation on the N_2 molecule and obtained as a result an energy gain of 3.25 eV, i.e. almost the same as above. In 1971 Mulliken and Liu[22] compared in the same calculation and by the same method the role of *d* corrections for N_2 and P_2. In particular, the energy gain for N_2 (2.58 eV) actually proved to be greater than for P_2 (2.53 eV).

It is clear from these investigations that the differences between the properties of elemental nitrogen and phosphorus are not associated with the contribution of *d* orbitals. Nevertheless the differences between N_2, an inert gas, which condenses at −196°C, and P_4, which is an extremely reactive crystalline substance, are very great. They can be accounted for in the following way. In the N_2 molecule, the σ bond is formed from compact orbitals and the optimum distance for their overlap is small. At this distance, the p_x orbitals overlap very markedly forming a strong π bond. A similar strong π bond is also formed by p_y orbitals. This results in a very stable N_2 molecule, in which the nitrogen atoms are linked by a strong triple bond. In phosphorus, the orbitals are much larger and much more diffuse than in nitrogen. The optimum distance for the formation of the σ bond is so great that π overlapping at this distance is very slight and π bonds are energetically unfavourable; this is why multiple bonds are altogether uncharacteristic of the elements of the Third Period. In the case of phosphorus, the formation of three single bonds with three adjacent atoms at the vertices of the tetrahedron is energetically more favourable than the formation of a triple bond in the P_2 molecule§. Admittedly, all these bonds are of the "banana" type, since the orbitals deviate from the bond axes. However, for large diffuse orbitals, this does not unduly impair the conditions for overlap.

Thus the differences between the properties of elemental nitrogen and phosphorus are due to the differences between the sizes of the orbitals.

We shall now consider tricoordinate compounds. We shall begin with the simplest examples: phosphine (PH_3) and ammonia (NH_3). Boyd and Lipscomb[20] carried out a calculation on the PH_3 molecule and found that the contribution of *d* orbitals is very significant. The importance of *d* orbitals for ammonia was established by Clementi and coworkers[23].

The values of the *d*-orbital corrections depend very strongly on the quality of the calculation. Thus in the calculation of Hillier and Saunders[24] the population of the *d*-type orbitals of phosphorus in PH_3 was 0.26*e*. On the other hand Rothenberg et al.[25] obtained 0.08*e* for this population in a more accurate calculation, which led them to the conclusion that the role of *d*-type orbitals is great in those cases where they compensate the defects of an inadequate *s*,*p*-basis set. Finally a comparison of PH_3 and NH_3 in a single calculation was carried out by Petke and Whitten[26], who found that the *d* corrections for ammonia are no less important than for phosphine and for this reason the *d* orbitals do not play a special role in PH_3. However, it may be that in phosphine *d* orbitals do not play a special role simply because of the lack of π-donor ligands. It is therefore necessary to examine calculations on molecules with such ligands. There are literature data for PF_3. Hillier and Saunders[27] obtained 0.71*e* for the population of the *d*-type orbitals in PF_3 and concluded that the population of the *d* orbitals of phosphorus increases with increase of the π-donor capacity of the ligands. However, calculation on this molecule using a much better approximation[28] yielded no population for *d* orbitals. Thus one may assume that in tricoordinate compounds the

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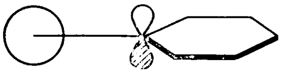
§These molecules exist only in the vapour phase.

role of *d*-type corrections for phosphorus and nitrogen is the same.

The different properties of these compounds are also caused by the sizes of the orbitals. Owing to the larger size of the valence orbitals of the phosphorus atom, its bonds are longer, which is very important for molecular geometry. A calculation was carried out in 1973 on ammonia[29], in which the N-H bond length has varied. For smaller bond lengths than the experimental value, the molecule was found to be planar; with increase of bond length, it became non-planar and the angle of the pyramid decreased. The angle reached the experimental value when the N-H bond length became equal to the experimental bond length. On further increase of bond length, the pyramid became increasingly sharp, the angle reaching 90° ultimately. In phosphine, the bonds are so long that the angle is almost 90°.

We shall now consider how the difference between the angles of the pyramid affects the properties of aromatic compounds, for example, aniline and phenylphosphine. The pyramid is flattened at the nitrogen atom and the lone electron pair has a greater amount of *p* character, i.e. it is virtually located in a *p* orbital. The N-C bond length is such that π overlapping is effective,

and there is conjugation between the electron pair and the ring, so that the nitrogen atom in aniline is a stronger donor. On the other hand, the N-H bonds are located in the plane of the ring and their orbitals cannot overlap with the p_Z orbitals of the carbon atom. Consequently, they hardly interact with the π-electron system of the benzene ring. In phenylphosphine, the valence angle is close to 90° and the orbital of the lone electron pair has almost pure *s* character. It cannot therefore interact with the antisymmetric p_Z orbitals of the carbon atom and there is no conjugation with the ring and no electron transfer to the latter:

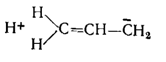
 .

However, one of the P-H bonds is formed by the p_Z orbital of the phosphorus atom, which may interact with the p_Z orbital of the carbon atom. Thus, in contrast to aniline, in phenylphosphine the bonds (and not the lone electron pair) interact with the benzene ring.

The concept of σ, π conjugation (hyperconjugation) is widely used in chemistry[30,31]. Hyperconjugation is understood as symmetry-allowed interaction of σ bonds with π-electron systems. The direction of the hyperconjugation effect depends on the polarisation of the σ bonds. The hyperconjugation effect of methyl groups is believed to be of the donor type and is represented by arrows

$$H_3{\equiv}C{-}CH{=}CH_2$$

or by resonance structures of the type

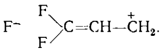
 .

$$H^+\ \ H_2C{=}CH{-}\bar{C}H_2$$

The hyperconjugation effect of trifluoromethyl groups is believed to be of the acceptor type and is represented by arrows

$$F_3{\equiv}C{-}CH{=}CH_2$$

or by resonance of structures of the type[32]



$$F^-\ \ F_2C{=}CH{-}\overset{+}{C}H_2.$$

The electronegativity of the phosphorus atom is less than that of the carbon atom and even less than that of oxygen, the halogens, etc. As a result the σ bonds of phosphorus with the substituents are polarised in the direction $P^{\delta+}-X^{\delta-}$. The σ,π conjugation with the σ bonds of phosphorus, can therefore be of the acceptor type. The reality of the hyperconjugation effects of both methyl[33] and trifluoromethyl[34-36] groups has been questioned in recent years. Indeed, the interaction of the very strong and compact C-H bonds and even more so the C-F bonds with π-electron systems should be so slight that it can hardly be a real cause of the phenomena for the explanation of which the hyperconjugation effect is invoked. For elements of the Third Period, the situation is different. The bonds of silicon, phosphorus, and sulphur are formed by the much more diffuse valence orbitals of these elements. For this reason, the strength of these bonds, their polarisability, and their mobility are comparable to the corresponding characteristics of π orbitals. This is why the effects of σ,π conjugation with the σ bonds of the elements of the Third Period should be observed.

Thus the acceptor properties of tricoordinate phosphorus can be explained by the size and diffuseness of its *s* and *p* orbitals and not by the presence of *d* orbitals in its valence shell. The change in the size of the valence orbitals led to a change in geometry, i.e. a change in conjugation conditions (conjugation with σ bonds and not with a lone electron pair), and to an increase in the extent of σ,π conjugation[37-39].

Using tetracoordinate phosphorus and nitrogen compounds as examples, one can conveniently explain what is understood by *d* corrections. In amine oxides the bond is believed to be semipolar and its formation is represented as follows. An electron passes from the nitrogen atom to oxygen. One unpaired electron, which remains in O^-, forms a σ bond with the quadrivalent ammonium nitrogen atom and the six other electrons (five from O and one from N) form lone pairs. Two of these are located in the p_X and p_Y orbitals, i.e. have π character. This description conveys only very approximately the real form of the electron cloud, since the form of the p_π orbitals of the oxygen atom in this cloud remains the same as in the isolated oxygen atom:

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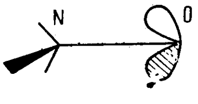
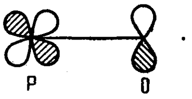
Furthermore, the molecule of the oxide contains the positively charged N^+ atom next to O^-. Under the influence of the positive charge, the electron cloud should be deformed and drawn into the region of the bond:

 .

The traditional description of amine oxides does not reflect this deformation. Here the attraction of the electron cloud to the region of the bond is represented with the aid of the *d* orbitals of the phosphorus atom. For example, it is assumed that the p_X orbital of the oxygen atom interacts with the d_{xz} orbital of the phosphorus atom and forms a π bond:

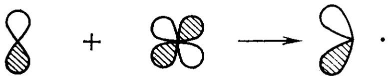


A similar bond is formed by the p_y orbital of the oxygen atom with the d_{yz} orbital of the phosphorus atom. Thus in phosphine oxides the linkage is partly of the triple bond type:

$$P \equiv O.$$

The attraction of the electron cloud into the region of the bond in amine oxides might be described in exactly the same way with the aid of fictitious d orbitals of nitrogen, since in the case of phosphorus one employs fictitious and not atomic d orbitals. However, this attraction in both phosphine and amine oxides can be represented in a different way. It is required that the form of the orbitals of the oxygen atom should be modified so that they become extended into the region between the atoms:

This can be achieved with the aid of the d orbitals of the oxygen atom. We combine the p_x orbital with an orbital of the d_{xz} type:



Naturally, the latter orbital has nothing in common with the atomic d orbitals: this is the so called polarisation correction and the admixture of the d-type orbital is postulated only in order to account for the change in the shape of the electron cloud. The particular atom in the molecule to which the polarisation correction is applied has no fundamental importance, since it is a purely formal procedure—it can be applied to phosphorus, nitrogen, and oxygen. Such calculations have not been made for oxides, but one cannot rule out the possibility that d orbitals in oxygen would give a good description of the change in the shape of the electron cloud. On the other hand, it is known that the d-orbital corrections for silicon hardly affect the results of calculations on silylamine, while the d-orbital corrections for nitrogen greatly improve the result.[40]

There are very few quantitative data for amine and phosphine oxides. Nevertheless Hillier[41] has carried out a calculation on the F_3PO molecule and obtained a high population of the phosphorus d orbitals (0.5e) in the PO bond. Choplin and Kaufmann[42] performed a calculation on the same molecule and on the oxide F_3NO without taking into account the d orbitals for the nitrogen atom. We mention this study, because its authors understood the necessity of including also the d orbitals for the nitrogen atom, although they were unable to do this for technical reasons. Frost et al.[43] carried out a calculation on the PO and NO linkages in the F_3PO and F_3NO molecules taking into account the d orbitals and obtained approximately equal contributions of the d orbitals for nitrogen and phosphorus atoms; however, they performed only a model calculation by the valence bond method. Unfortunately comparable non-empirical calculations on amine and phosphine oxides have not so far been made.

It must be emphasised that the differences in the chemistry of nitrogen and phosphorus compounds are to a large extent determined by the ease of formation of the phosphoryl linkage, i.e. its greater strength. The illusory nature of the traditional explanation of the comparative strength of the PO linkage and its triple bond character was demonstrated above. It is reasonable to suppose that the increased tendency of the lone electron pair of the phosphorus atom towards oxidation is determined mainly by the properties of the initial lone pair and not of the oxide linkage formed. The electrons of the compact lone pair of the nitrogen atom are comparatively more strongly attracted to the nucleus, which increases the energy expenditure on the removal of the electron and makes the formation of the N-oxide linkage less favourable compared with the phosphoryl linkage and makes it weaker.

These considerations can be confirmed by a comparison, using a fairly clear-cut example, of the ionisation potentials of the lone pairs with the strengths of the oxide linkages formed in analogous phosphorus and nitrogen compounds. It is difficult to compare the hydrides owing to the large differences between the geometries and the associated differences between the hybridisations of the lone pairs. Comparison of alkyl and particularly aryl derivatives is hindered by the appreciable delocalisation of the lone pair of the nitrogen atom in these compounds. Fluorides are the most suitable for the comparison, since the differences between their geometrical structures and hence between the hybridisations of the lone pairs are slight ($\angle FPF \simeq 98°$, $\angle FNF \simeq 102°$) and the changes in geometry on oxidation are also small ($\Delta\angle FPF \simeq +3.5°$, $\Delta\angle FNF \simeq -1.2°$).[142] Owing to the exceptionally high electronegativity of fluorine, the ionisation potential in this instance can be attributed to the lone pair with a greater degree of justification than for any other substituents. The ionisation potential of NF_3 does indeed exceed that of PF_3 by 80 kcal mole^{-1}. It is not therefore surprising that the PO linkage in F_3PO is much stronger than the NO linkage in F_3NO (by more than 30 kcal mole^{-1}). Thus in this case too the differences between the properties are ultimately determined by the differences between the sizes of the valence orbitals of the nitrogen and phosphorus atoms.

We shall now turn to penta- and hexa-coordinate compounds. Santry and Segal[15] carried out a calculation on the PF_5 molecule and obtained a population of the d orbitals of the phosphorus atom equal to 1.6e. Later Brown and Peel[44], made a similar calculation, obtained a population of the phosphorus d orbitals of 0.3e, and concluded that there is no reason for invoking d orbitals in order to describe the electronic structure of this molecule. Highly accurate non-empirical calculation on the PH_3F_2 molecule and the hypothetical PH_5 and NH_3F_2 molecules have been published recently[45]. The authors concluded that the stability of the PH_3F_2 and PF_5 molecules can be accounted for without invoking d orbitals and that the decisive factor responsible for the stability of the PH_3F_2 molecule, on the one hand, and the instability of NH_3F_2, on the other, is the difference between the ionisation potentials of the planar PH_3 (7.8 eV) and NH_3 (10.3 eV) species. On the other hand, the authors[45] note that the energy gain following the expansion of the basis set by including d-type orbitals and the population of these orbitals are greater for PH_3F_2 than for NH_3F_2. However, it must be emphasised that the roles of the d-orbital corrections were compared for a configuration which is stable in one of the molecules (PH_3F_2) and unstable in the other (NH_3F_2). Indeed, when the basis set was expanded by including *d*-type orbitals in the nitrogen atom, it was found that the stable configuration of NH_3F_2 is of the C_{3v} type, corresponding to the tetrahedral ammonium cation NH_3F^+ and the F^- anion associated with it by purely electrostatic forces, and not a trigonal bipyramid (D_{3h}) as in the PH_3F_2 molecule. The latter result suggests in addition that the differences between PH_3F_2 and NH_3F_2 are associated with steric hindrance (see below).

A calculation has been performed on the PF_6^- anion[46], which yielded an appreciable population of the *d* orbitals (1.2*e*). However, exactly the same calculation on SF_6 yielded a charge of $-0.3e$ on the sulphur atom. It is unlikely that the sulphur atom surrounded by fluorine atoms should have a negative and not a positive charge. Thus, from the chemical standpoint alone, the *d*-orbital population in this calculation is much too high. On the other hand, theoretical analysis demonstrates the necessity for a high population of the *d* orbitals of the central atom in octahedral molecules[47]. One must therefore expect that, in the calculation by the same method on the octahedral NF_6^- anion, a high population of the *d* orbitals would also have been obtained for the nitrogen atom. Unfortunately a calculation on this hypothetical anion has not been made.

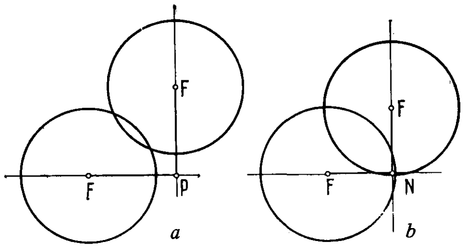


Figure 9. Comparison of the P–F (*a*) and N–F (*b*) bond lengths with the van der Waals radius of the fluorine atom.

We shall now consider why the anion does not exist. Fig. 9*a* illustrates the P–F bond length and the van der Waals radius of the fluorine atom. Evidently fluorine atoms hardly overlap and only a slight increase in bond length is required for the disappearance of steric hindrance to the formation of the molecule; at the same time, the diffuse phosphorus orbitals are relatively insensitive to a slight increase in bond length. Fig. 9*b* illustrates the same situation for the nitrogen atom. Evidently fluorine atoms overlap very strongly. In order to eliminate steric hindrance, it is necessary to extend the N–F bond to such an extent that it is ruptured. In other words, penta- and hexa-coordinate compounds of nitrogen cannot exist owing to considerable steric hindrance. Consequently penta- and hexa-coordinate compounds of phosphorus exist simply because its atom is sufficiently large to accommodate five (or six) ligands around it and not because it has a *d* orbital available for the formation of additional linkages. Therefore, bonding in these compounds can be accounted for, as shown above, without invoking *d* orbitals.

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Thus the differences between the properties of phosphorus and nitrogen compounds can be explained by a very simple but very important factor: the difference between the effective sizes of the *s* and *p* orbitals of the nitrogen and phosphorus atoms.

The presence of vacant *d* orbitals in the valence shell of the phosphorus atom can in no way influence the properties of phosphorus compounds, since these orbitals are so unfavourable energetically and so diffuse that they are incapable of any appreciable interaction with other valence orbitals.

d Orbitals can play the role of polarisation corrections, which is important from the standpoint of the method of calculation but has almost no chemical importance or no chemical importance whatsoever. As far as one can judge, from the available data, the roles of these corrections for nitrogen and phosphorus are approximately the same.

In view of the identical orders of magnitude of the *d*-orbital corrections in the case of nitrogen and phosphorus, the concept of *d* orbitals cannot be used correctly as a language suitable for the description of the differences between the properties of compounds of these elements.

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Molecular Rearrangements in the Series of Carane Derivatives

B.A.Arbuzov and Z.G.Isaeva

The available information about the molecular rearrangements of carane derivatives in addition, elimination, and substitution reactions are examined and the structural and steric principles which determine the nature of the rearrangements are analysed. A systematic account is given of data concerning the changes in the carane structure in various reactions involving rearrangements with participation of three-membered and six-membered rings.
The bibliography includes 100 references.

CONTENTS

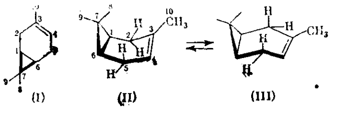
I. INTRODUCTION

Extensive factual data have now accumulated on the chemistry of bicyclic terpene derivatives of the carane series. Since the beginning of the 1960's, the stereochemistry of carane derivatives has been investigated vigorously, largely as a result of the application of various physical methods for the study of steric structure and the principles of conformational analysis. In the course of this research, numerous stereoisomeric carane derivatives have been synthesised, their configurations and conformations have been elucidated, and extensive information has been obtained about their reactivities. Data concerning the transformations of carane derivatives in various reactions have been partly surveyed in a number of reviews[1,2], but the results of stereochemical investigations on caranes have not yet been described systematically.

The present review deals with publications in the last ten years containing information about the molecular rearrangements of carane derivatives in addition, elimination, and substitution reactions, and analyses the structural and steric principles which determine the nature of the rearrangements.

II. THE STERIC STRUCTURES AND STEREOISOMERISM OF CARANE DERIVATIVES

The results of studies on the photosensitised oxygen-transfer reaction and an examination of Dreiding models have led to the hypothesis[4,5] that 3-carene (I)† molecules can exist in an equilibrium 1 : 1 mixture of two "boat" forms (II) and (III):

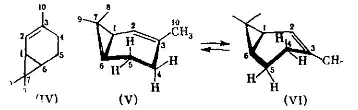


(I) (II) (III)

It follows from electron diffraction data[6] that the *syn*-boat conformation (II) exists. Examination of the ^{1}H NMR spectra demonstrated the possibility that 3-carene molecules exist as a mixture of two conformers, again with the *syn*-boat form (II) predominating[7,8].

On the basis of the results of a study of the conformational structure by the method of molar Kerr constants and of calculations of the energy difference between the conformers, taking into account steric and electrostatic interactions, Vereshagin and Vul'fson[9] concluded that conformer (II) predominates (to an extent of at least 90%) in the equilibrium mixture of (II) and (III). Despite its being sterically "filled" from the inner or *p*-side, the stability of form (II) has been accounted for[7] by the absence of a rigid interaction between the non-bonded 8-CH_3 group and the *p*-hydrogen atoms at $C_{(2)}$ and $C_{(5)}$, which is present in the boat form (III).

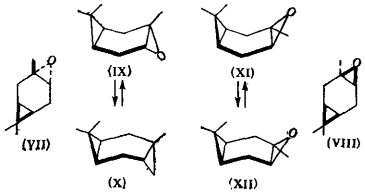
The conformation of the isomeric 2-carene (IV) was determined in a similar way. Of the two possible conformations (V) and (VI), the partial boat form (V) is preferable[7,10]:



(IV) (V) (VI)

It is seen from Dreiding models that the interatomic distance between 8-CH_3 and 4β-H in conformer (VI), amounting to 0.2 Å, is responsible for the steric hindrance in the molecule, which makes this conformation unfavourable. The results of the analysis of the steric interactions of the atoms on the basis of the correlations between the spin-spin coupling constants and the dihedral angles led to the adoption of conformation (V) also for 2-carene and its 4-substituted derivatives[11]. Arbuzov et al.[12] explained why conformation (V) is preferable by analysing the relative chemical shifts of the protons of the *gem*-dimethyl groups using dipole moments and molar Kerr constants.

The configurations and conformations of the stereoisomeric 3,4-epoxycaranes (VII) and (VIII) and of 2,3-epoxycarane (XIII) have been determined with the aid of the same set of methods for the investigation of steric structure[8,9,12-16].



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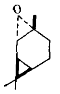
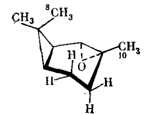
† In this review the carane system is numbered in accordance with the IUPAC nomenclature[3].

As for the corresponding olefin (I), conformations with the six-membered ring in the *syn*- and *anti*-boat forms are possible for the stereoisomeric 3,4-epoxycaranes. Form (IX) predominates in the equilibrium mixture of the conformers of the α- or *trans*-isomer (VII)(with respect to the steric orientation of the three-membered ring relative to the plane of the cyclohexane ring)[8,15]. Completely unanimous conclusions have not been reached concerning the choice of the preferred conformation of the β- or *cis*-isomer (VIII).[8,15-17]

α-2,3-Epoxycarane (XIII) has the partial boat conformation (XIV):[12]

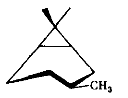


(XIII)

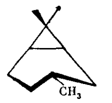


(XIV)

It is evident from an examination of Dreiding models and ^{1}H NMR spectra of the stereoisomeric saturated *cis*- and *trans*-caranes‡ that their most probable steric structures must be the half-chair conformations (XV) and (XVI) with the equatorial (*e*) 10-CH$_3$ group[18]:

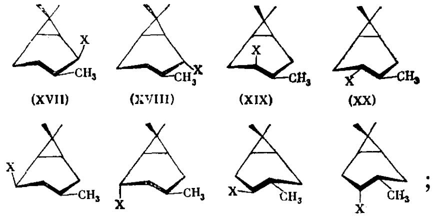


(XV)



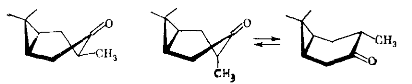
(XVI)

It has been shown by ^{1}H NMR spectra that the amines of the *cis*-carane series, stereoisomeric with respect to the position of the NH$_2$ group and the carbon atoms of the six-membered ring, have the half-chair conformation (XVIIIa–XXIIa), with rare exceptions[19]:

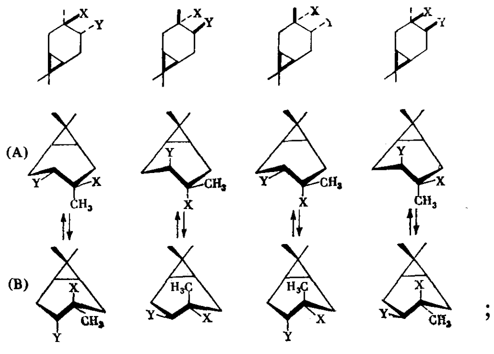


(a) X = NH$_2$; (b) X = OH .

In studies on the stereochemical structures using both physical and chemical methods, the half-chair conformation with the *e*-10-CH$_3$ group (XVIIb–XXIIb) was assigned to the isomeric secondary alcohols of the *cis*-carane series[20]. Preferred half-chair conformations have been found also for the stereoisomeric *trans*-4-caranols (XXIIIb, XXIVb).[14] Different conformations have been proposed for the two stereoisomeric 4-caranones (based on the results of studies by ^{1}H NMR and optical rotatory dispersion[14], dipole moment, and Kerr effect[21] methods and an examination of models): half-chair with the *e*-10-CH$_3$ group [form (XXV)] for the *cis*-isomer and a conformer intermediate between the half-chair with an axial (*a*) 10-CH$_3$ group [form (XXVI)] and a boat with the *e*-10-CH$_3$ group for the *trans*-isomer:



Calculations (based on Kitaigorodskii's mechanical model) on the equilibrium optimal conformations of the four isomers of carane-3,4-diol[22], two *trans*-3,4-dichlorocaranes[23], and *trans*-4-bromo-3-hydroxycarane[24], also led to the assumption that the half-chair conformation is preferred for the six-membered carane system of these compounds and it has been shown that 3,4-disubstituted caranes (XXVIII–XXXI) can exist in the form of equilibrium mixtures of conformers (A) and (B).

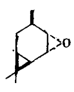


(a) X=Y=OH; (b) X=Y=Cl; (c) X=OH, Y=Br; (d) X=OH, Y=OAc; (e) X=OH, Y=OTs; (f) X=Hal, Y=OAc; (g) X=Y=Br; (h) X=OH, Y=Cl.

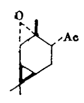
Similar results were obtained in a study of 3,4-dihalogencaranes from dipole moments and Kerr effects[25,26] and of carane-3,4-diols, their monoethers, and ketols by infrared spectroscopy (an intramolecular hydrogen bond was detected)[27,28].

The conclusions concerning the steric structure of carane derivatives agree with the steric relations governing the occurrence of the corresponding reactions. In this respect carane derivatives have proved to be convenient objects for the elucidation of the stereochemical aspects of particular reactions, for the investigation of reaction mechanisms, since they make it possible to make comparative estimates of the influence of electronic, configuration, and conformation factors.

One of the characteristic features of the stereochemistry of carane derivatives is the stereospecificity of electrophilic addition to isomeric carenes having a double bond within the tricyclic system. In all the reactions investigated hitherto the double bond of carenes is attacked by the electrophilic species in the *trans*-position (or from the "α-side") with respect to the *endo*-condensed cyclopropane ring. Thus the only products of epoxidation by peracids are the *trans*-isomers (with respect to the mutual orientation of the three-membered rings) of epoxycaranes[11,12,14,29-33] (VII), (XIII), and (XXXII) and 4α-acetyl-2α, 3α-epoxycarane[34] (XXXIII).



(XXXII)



(XXXIII)

Reactions involving photosensisised oxygen transfer to carenes[4,32], oxidative hydroboration of carenes[10,14],

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‡The conformational relations of carane derivatives are determined, on the one hand, by the mutual disposition of the 10-CH$_3$ group and the three-membered ring relative to the plane of the cyclohexane ring and, on the other hand, by the steric orientation of the functional groups in relation to the three-membered ring. Carane derivatives can be divided into two series, with *cis*- and *trans*-carane structures, on the basis of the type of the hydrocarbon skeleton.

hydroxylation with KMoO$_4$ and OsO$_4$–H$_2$O,[8,22,35] Friedel–Crafts acetylation, and the Prins reaction[11] lead to the formation of products with the α- (or *trans*-) orientation of the functional groups. Such stereospecificity of the attack on the double bond of carenes is caused, as can be seen from Dreiding models, by the hindered approach by the bulky electrophilic agents from the β-side shielded by the 8-CH$_3$ group.

A second distinctive feature of the behaviour of carane derivatives is a tendency towards a rearrangement of the hydrocarbon skeleton of the carane in different reactions.

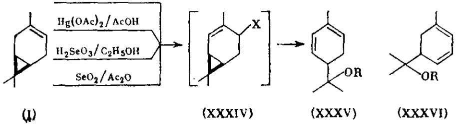
III. MOLECULAR REARRANGEMENTS OF THE CARANE STRUCTURE

The possibility of skeletal rearrangements due to the involvement of both rings is inherent in the very structure of the carbon system of carane, which contains condensed alkyl-substituted six- and three-membered rings.

1. HOMOALLYL REARRANGEMENTS

(a) Rearrangement Involving the Conjugated System of a Double Bond and the Cyclopropane Ring

The first evidence for the possibility of an allyl type of rearrangement of 1,3-diene systems in the series of carane derivatives was obtained in a study of the oxidation of 3-carene by Pb(OAc)$_4$, Hg(OAc)$_2$, and H$_2$SeO$_3$ under various conditions[36-39]. In all cases one of the main reaction products proved to be the ester of the dienol of the *p*-methane series (XXXV); the reaction with Pb(OAc)$_4$ also gave the ester of the dienol of the *m*-menthane series (XXXVIb):



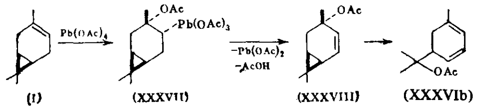
(I) (XXXIV) (XXXV) (XXXVI) ;

(1) X=Pb(OAc)$_3$
(2) X=HgOAc
(3 and 4) X=SeO$_2$H

(a) R=H
(b) R=Ac
(c) R=Et .

The conversion of 3-carene into *p*-menthadienol derivatives under the influence of these agents has been explained by postulating the intermediate formation of allyl-substituted 2-carene derivatives of the elements of type (XXXIV), the solvolysis of which is accompanied by the allyl rearrangement with participation of the vinyl cyclopropane fragment.

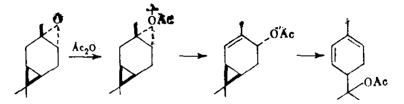
In order to convert olefins into acetates derived from allyl alcohols under the influence of Pb(OAc)$_4$, one can use also another pathway, involving the formation of an adduct of the olefin and Pb(OAc)$_4$ as an intermediate[40]. Accordingly, the oxidation of 3-carene with Pb(OAc)$_4$ should lead to the acetate of *m*-mentha-4,6-dien-8-ol (XXXVIb)[41,42] via the mechanism of the "4-carene → *m*-mentha-4,6-diene" rearrangement:



(I) (XXXVII) (XXXVIII) (XXXVIb) .

According to Whitham[43], Pb(OAc)$_4$ forms a *cis*-adduct with olefins. The adduct (XXXVII) is converted, with liberation of Pb(OAc)$_2$ and an AcOH molecule, into the acetate of *cis*-car-4-en-*trans*-3-ol (XXXVIII), which rearranges to (XXXVIb) under the reaction conditions.

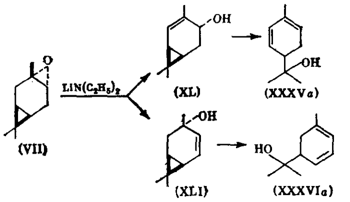
The formation of compound (XXXVb) from α-3,4-epoxycarane (VII) in the reaction with acetic anhydride has been explained similarly[44,45]:



(VII) (XXXIX) (XXXVb) .

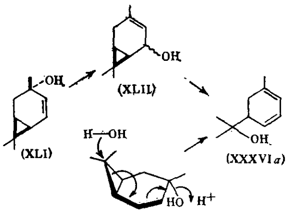
The identification of car-2-en-*trans*-4-ol (XXXIX) together with compound (XXXVb) in the products of these reactions was regarded as evidence for the possibility of the "2-carene → *p*-mentha-1,5-diene" rearrangement. The two isomeric products (XXXVb) and (XXXIX) were also identified in the products of the reaction of 3β,4α-dihalogenocaranes with AgOAc in acetic acid[46,47].

Presumably the rearrangement investigated occurs in the reaction of the allylic carenols (XL) and (XLI) (the products of the isomerisation of α-3,4-epoxycarane by a base[49]) with phthalic anhydride[49]; the rearranged alcohols were identified in the reaction mixture.



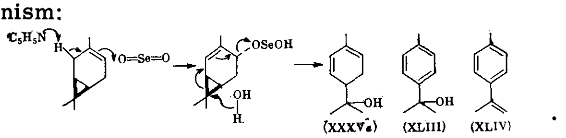
Thus in the examples quoted above the allyl rearrangements involving the vinylcyclopropane fragment were observed only indirectly. The "4-carene → *m*-mentha-4,6-diene" rearrangement has been achieved directly.

Gollnick et al.[50] showed that car-4-en-*trans*-3-ol (XLI) is converted quantitatively into *m*-mentha-4,6-dien-8-ol (XXXVIa) on refluxing with water and under the influence of acetic or dilute sulphuric acid at room temperature.

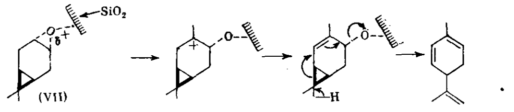


Gollnick et al.[50] suggested that this transformation can occur either as a concerted process or via car-3-en-5-ol (XLII), which undergoes a homoallyl rearrangement with participation of the cyclopropane ring under the reaction conditions.

According to the latest report by Cocker and coworkers[51], the oxidation of 3-carene by SeO$_2$ in pyridine (after refluxing for 3 h) with subsequent steam distillation of the reaction products yields preferentially compounds of the *p*-menthane series (XXXVa) (50%) and its degradation and dehydration products 2-(*p*-tolyl)-2-propanol (XLIII) (11%) and *p*-isopropenylmethylbenzene (XLIV) (11%). The authors explain their formation from 3-carene by the "interference" of the "2-carene → *p*-mentha-1,5-diene" rearrangement occurring analogously[50] to the concerted mechanism:

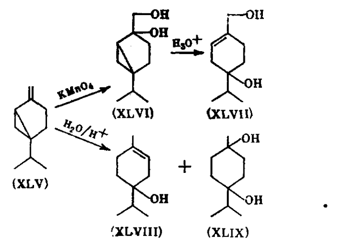


There is an interesting interpretation[52] of the transformations of *α*-3,4-epoxycarane (VII) under the influence of silica gel, which is regarded as a matrix with an electron-accepting surface responsible for the carbonium mechanism of the process; one of the pathways in the reactions involves a rearrangement similar to that already described above



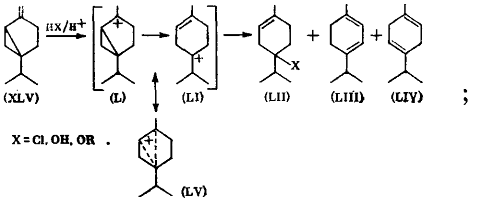
(b) Homoallyl Rearrangement with Participation of the Cyclopropane Ring

The homoallyl rearrangement in the series of bicyclic terpenes was observed previously for derivatives of bicyclo[3,1,0]hexane with a system of condensed three- and five-membered rings. Thus Semmler[53] found that the hydroxylation of Sabinene (XLV) by $KMnO_4$ leads to the diol (XLVI), which readily isomerises to the diol (XLVII) under the influence of dilute H_2SO_4 in the cold:



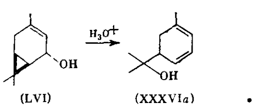
The hydration of sabinene (XLV) with 10% H_2SO_4 also leads to the monocyclic products (XLVIII) and (XLIX).[54]

Goryaev and coworkers[55–57] obtained analogous results in the study of the transformations of sabinene (XLV) in reactions with HCl—the hydration and alcohol addition reactions in an acid medium:

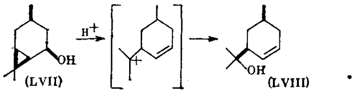


It is evident from the above scheme that the formation of monocyclic products is the result of the rearrangement of the cyclopropylmethyl ion (L) to the homoallylcyclohexyl ion (LI) and the stabilisation of the latter by the attack of a nucleophile to give the terpenen-4-ol ether (LII) or the ejection of β-H^+ leading to the hydrocarbons (LIII) and (LIV). The authors also believe that the hydration of sabinene via the non-classical ion (LV) is probable.

In the carane series, the rearrangement of the cyclopropylmethyl derivative to the homoallyl compound was also achieved somewhat later by the conversion of car-3-en-*trans*-5-ol (LVI) into *m*-mentha-4,6-dien-8-ol (XXXVIa):[32]



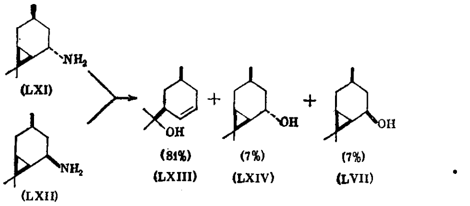
According to the data of Cocker and coworkers[58], *cis*-caran-*cis*-5-ol (LVII) partly isomerises to *cis*-*m*-menth-4-en-8-ol (LVIII) under the influence of dilute hydrochloric acid at room temperature or on heating with acetic acid in sealed tubes:



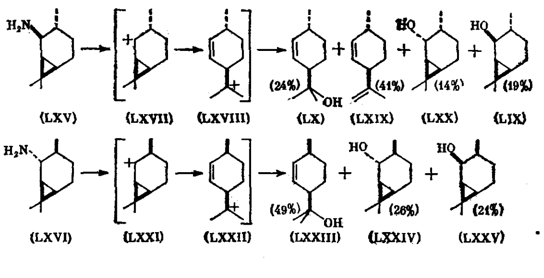
The rearrangement (LVII) → (LVIII) has also been noted under the conditions of the oxidation of compound (LVII) with chromic acid, particularly in oxidation in 75% acetic acid; in acetate buffer (pH 2.24), the rate of rearrangement is insignificant[20].

The homoallyl rearrangement has also been observed for *trans*-caran-*cis*-2-ol (LIX),[59] which is converted into *trans*-*p*-menth-2-en-8-ol (LX) under the conditions mentioned above for *cis*-caran-*cis*-5-ol (LVII):

More complete data on the rearrangement of cyclopropylmethyl derivatives were obtained by Cocker and coworkers in a study of the deamination of stereoisomeric amines of the carane series[60]. The deamination of the epimers (LXI) and (LXII) leads preferentially to the rearrangement of the product (LXIII), the composition of the deamination products being independent of the configuration of the initial amine:



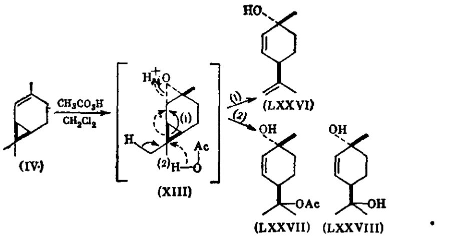
Stereoisomeric 2-amines with the *trans*-carane structure (LXV) or the *cis*-carane structure (LXVI) give a mixture of products having various compositions (different from those obtained previously); in this case the content of the rearranged products is smaller.



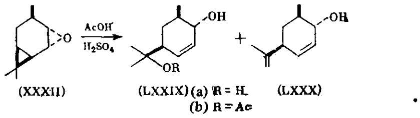
The authors explain the difference on the hypothesis that steric and electronic factors influence the ease of the rearrangement. While the formers promote to an equal extent the rearrangement of the corresponding α-cyclopropylcarbonium ions, with migration of the carbonium ion centre to a side chain, the influence of the electronic factors must be different, Owing to the $+I$ effect of the 10-CH_3 group in compounds (LXVII) and (LXXI), which stabilises the positive charge on the 2-C atom, there is an increase of the possibility of the formation of the non-rearranged products (LIX), (LXX), (LXXIV), and (LXXV). For the isomeric amines (LXI) and (LXII), the formation of the rearranged product (LXXIII) should be the dominant process.

Thus expansion of the range of isomeric carane derivatives investigated and the extension to them of the reactions accompanied by the formation at some stage of an electron-deficient centre in the α-position relative to the cyclopropane ring made it possible to observe directly in a number of instances their homoallyl rearrangement. The observations were used to elucidate the mechanism of the reactions, the pathways followed in the formation of particular products, and hence individual reaction pathways.

In an attempt to synthesise α-2,3-epoxycarane (XIII) by the epoxidation of 2-carene with peracetic acid, Gollnick and Schade[32] isolated *cis*-*p*-mentha-2,8-dien-1-ol (LXXVI), which they regard as the product of the acid-catalysed isomerisation of the α-2,3-epoxycarane (XIII) formed initially:

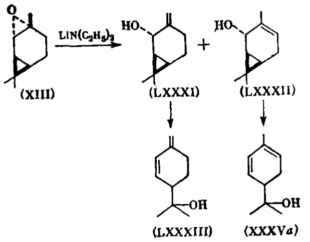


The rearrangement of α-2,3-epoxycarane (XIII) under the conditions of the epoxidation of 2-carene (IV) by a solution of peracetic acid in a mixture of acetic acid and methylene chloride buffered with sodium acetate was reported somewhat later[61]. The reaction products consisted of a mixture of compound (LXXVI) and the monoacetate of *cis*-*p*-menth-2-ene-1,8-diol (LXXVII). The diol (LXXVIII) was isolated as the sole product of the hydration of the epoxide (XIII) by 1% sulphuric acid[62]. It has been shown[32,61,63] that α-4,5-epoxycarane (XXXII) can be obtained by the epoxidation of *cis*-4-carene, which rearranges just as readily under the influence of acids; in the reaction with acetic acid, even in the cold (0°C), it gives the monoacetate of *m*-menth-4-ene-6,8-diol (LXXIXb) and *cis*-*m*-mentha-4,8-dien-6-ol (LXXX) as the main products:

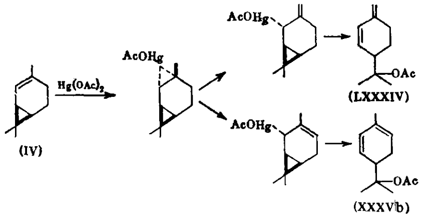


The diol (LXXIXa) has been obtained by Chabudzinski and coworkers[61,63] by treating the epoxide (XXXII) with 1% sulphuric acid, although the authors regarded it as carane-4,5-diol.

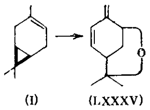
It is interesting to note that both allyl and homoallyl alcohols (LXXXI) and (LXXXII), the products of the isomerisation of α-2,3-epoxycarane (XIII) by $LiN(C_2H_5)_2$, rearrange even under the conditions of gas-liquid chromatography in a column with 10% of polyethylene glycol adipate on refractory brick at 140°C.[64] The carenols (LXXXI) and (LXXXII) rearrange rapidly in boiling water:



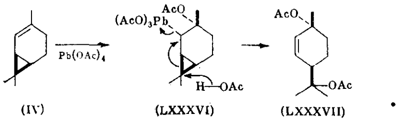
A study of the oxidation of 2-carene (IV) by $Hg(OAc)_2$ in acetic acid[65] showed that the formation of *p*-menthadienyl acetates (XXXVb) and (LXXXIV) involves a similar rearrangement at the stage where allylmercury acetates are solvolysed:



One cannot rule out the possibility that the formation of 2,8-oxy-*p*-mentha-1(7),5-diene (LXXXV) from 3-carene (I) when the latter is oxidised by SeO_2 in acetic anhydride[39,66] is also associated with the homoallyl rearrangement in the α-cyclopropylmethyl system:

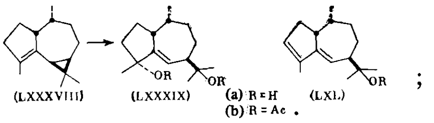


Assuming the homoallyl rearrangement at the stage involving the decomposition of allylic organolead intermediates, one can explain also the formation of the association complexes of the acetates (XXXVb) and (LXXXIV) in the oxidation of 2-carene (IV) by $Pb(OAc)_4$ in benzene[62]. As already mentioned, in agreement with the proposed mechanism[40], the oxidation of 2-carene by $Pb(OAc)_4$ can also proceed via another pathway involving an intermediate adduct (LXXXVI) of the olefin and $Pb(OAc)_4$. During its subsequent reactions, conditions also arise for the homoallyl rearrangement with opening of the cyclopropane ring and the formation of a monocyclic adduct:



In this case the acetate of *cis*-*p*-menth-2-ene-1,8-diol (LXXXVII) was identified in the reaction products.

It is of interest to compare the reactions involving the epoxidation and oxidation by $Pb(OAc)_4$ and SeO_2 of 2-carene (IV) and α-gurjunene (LXXXVIII), which contains the same vinylcyclopropane fragment as 2-carene (IV), but the latter is located in neighbouring rings[67-69]:

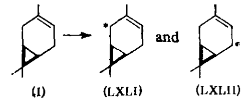


(LXXXVIII) (LXXXIX) (LXL)

(a) R = H
(b) R = Ac .

Comparison of the products of the above reactions of compounds (LXXXVIII) and (IV) demonstrates their fairly complete similarity.

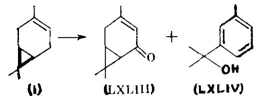
Under the influence of "allylic" oxidants, the "cyclopropylmethyl" fragment may arise in the 3-carene molecules in two ways:



(I) (LXLI) (LXLII) .

Presumably investigators encountered the rearrangement of the bicyclic 3-carene system to the *p*-menthadiene system, i.e. the rearrangement "2-carene → *p*-mentha-1,5-diene", already in the study of the catalytic autoxidation of 3-carene[70-72]. On the other hand, the structures of the corresponding rearranged reaction products were not finally elucidated, although it was shown subsequently that *p*- and *m*-menthadienols (XXXVa) and (XXXVIa) are formed as a result of the homoallyl rearrangement of the corresponding 3-carenyl derivatives (LXLI) and (LXLII) under the reaction conditions or during the separation of the reaction mixtures.

Cocker and coworkers[73], who investigated the oxidation of 3-carene by $KMnO_4$, found that the neutral products contain, apart from the main component car-3-en-5-one (LXLIII), also 8-hydroxy-*m*-cymene (LXLIV):

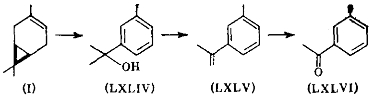


(I) (LXLIII) (LXLIV)

According to the results of Cocker and coworkers[74], compound (LXLIV) constitutes the bulk of the neutral oxygen-containing products of the oxidation of 3-carene by CrO_3 in acetone. However, when an acetone solution of CrO_3 buffered by sodium acetate is used, the yield of compound (LXLIV) is reduced by a factor of 2 and in pyridine by a factor of 4. Consequently, in an acid medium the stage responsible for the formation of compound (LXLIV) may involve the homoallyl rearrangement with opening of the three-membered ring.

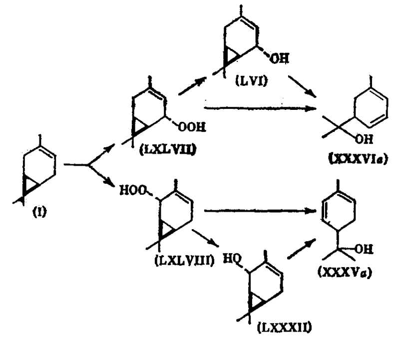
The same dependence of the yield of the rearranged products on the acidity of the medium was found in a study of the oxidation of 3-carene by t-butyl chromate[75,76].

The oxidation products of the *m*-series are represented by 8-hydroxy-*m*-cymene (LXLIV), 1-isopropenyl-3-methylbenzene (LXLV), and 3-methylacetophenone (LXVI). Their overall content in the reaction products reaches 70% when the oxidation reaction is carried out in a mixture of benzene, acetic acid, and acetic anhydride.



(I) (LXLIV) (LXLV) (LXLVI) .

The autoxidation of 3-carene in the presence or absence of a catalyst (cobalt stearate), using several methods for the reduction of the mixture of hydroperoxides formed initially, has been reinvestigated in detail by Baines and Cocker[51]. The products of the homoallyl rearrangement are represented by the *p*- and *m*-menthadienols (XXXVa) and (XXXVIa), their ratio depending primarily on the autoxidation reaction conditions: in the presence of a catalyst, a 1 : 4 mixture is formed, while in its absence the product is a 4 : 5 mixture with an increase of the overall yield of the two isomers by a factor of 2. Thus the preferential formation of products of the *m*-menthane series is evidence for the preferential attack on the 5-CH_2 group of 3-carene. The homoallyl rearrangement can occur in the reduction of carenyl hydroperoxides (LXLVII) and (LXLVIII):



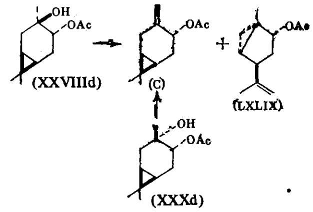
(I) (LXLVII) (LVI) (XXXVIa) (LXLVIII) (LXXXII) (XXXVa)

There is also the possibility of a rearrangement of the carenols (LVI) and (LXXXII) under the influence of an acid medium.

2. REARRANGEMENT WITH TRANSANNULAR CYCLOPROPYL PARTICIPATION

As in the homoallyl rearrangement, data concerning the transannular cyclopropyl participation in the chemistry of carane compounds have been obtained comparatively recently, although many such instances are known for the related bicyclic derivatives of the thujane series[77,78].

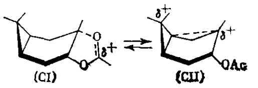
In 1966, Kropp[8,79] found that one of the products of the degradation of the monoacetate of carane-3-β,4α-diol (XXVIIId) by $POCl_3$ in pyridine has the structure of the acetate of 4-isopropenyl-1-methylbicyclo[3,1,0]-hexan-*trans*-2-ol (LXLIX):



(XXVIIId) (C) (LXLIX) (XXXd) .

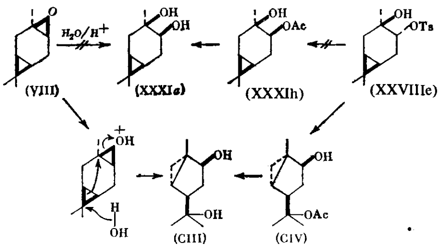
The degradation of the monoacetate of the stereoisomeric carane-3α,4α-diol (XXXd) under the same conditions yields only the acetate of car-3(10)-en-*trans*-4-ol (C) without appreciable admixtures of compound (LXLIX). Having compared the dehydration products of the two carane-3,4-diol ethers epimeric with respect to the 3-C atom, Kropp suggested that the condition determining the rearrangement with 1,3-transannular cyclopropyl participation is the *cis*-orientation of the eliminated OH group with respect to the cyclopropane ring. However, the absence of a rearrangement in the analogous dehydration of "model" epimeric alcohols, i.e. *trans*- and *cis*-3-caranols, showed that this condition alone is insufficient.

The formation of compound (LXLIX) and hence the occurrence of the rearrangement was interpreted by Kropp on the assumption of the equilibrium conformation (CI) ⇌ (CII) for the intermediate homocyclopropyl derivative in which the involvement of the cyclopropyl group is facilitated by the presence of the acetoxy-group, which "fixes" the six-membered ring of (CI) in the *syn*-boat conformation:



(CI) (CII) .

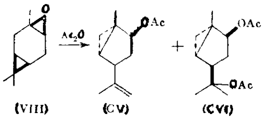
Having analysed the data available at the time on the transformations of the carane structure, Kropp concluded that the rearrangement constitutes the "first 'documented' example of the transannular cyclopropyl participation in the chemistry of carane". However, this rearrangement was presumably achieved in 1962 by Chabudzinski and Kuczynski[80] (who failed to notice it) in the hydration of β-3,4-epoxycarane (VIII) in an acid medium:



They erroneously attributed the structure of carane-3β,4β-diol (XXXIa) ("*cis*-carane-3,4-diol") to one of the two diols obtained in this reaction, having "confirmed" it by synthesis via the acetolysis of the monotosylate of carane-3β,4α-diol (XXVIIIe). It was subsequently found by the present authors[81] that the relevant diol has the structure of 4-(α-hydroxyisopropyl)-1-methylbicyclo[3,1,0]hexan-*cis*-2-ol (CIII). Consequently a rearrangement with the 1,3-transannular cyclopropyl participation occurred in both the hydration of β-3,4-epoxycarane (VIII) and in the acetolysis of the monotosylate (XXVIIIe); because of this coincidence, the rearrangement was not noticed.

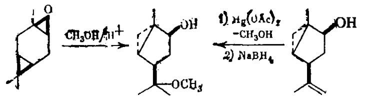
In connection with the elucidation of this finding, it became necessary to reanalyse the experimental data of the studies where "*cis*-carane-3,4-diol" had been identified[80]. As a result, the rearrangement with transannular cyclopropyl participation was observed in the reactions of 3β,4α-dibromocarane with Ag_2O,[82,83] or 3β,4α-dichlorocarane with AgOAc,[47] and of β-3,4-epoxycarane with $NaHSO_3$ in an aqueous solution[84].

In a study of the reaction of β-3,4-epoxycarane (VIII) with acetic anhydride, it was found[85,86] that approximately 50% of the mixture of reaction products consists of the acetates of 4-isopropenyl-1-methylbicyclo[3,1,0]hexan-*cis*-2-ol (CV) and the corresponding diol (CVI):



(VIII) (CV) (CVI) .

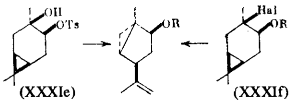
According to the results of Arbuzov et al.[87], the reaction of β-3,4-epoxycarane with methanol in the presence of an acid gives a low yield of the monoether (CIII) of the diol (CVII); the structure of compound (CVII) was confirmed by a synthesis involving hydration using the method of Arbuzov et al.[89]:



(VIII) (CVII) (CVIII) .

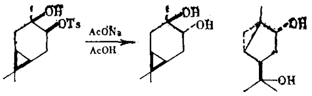
It is therefore of interest to note that one of the adducts of β-3,4-epoxycarane with methanol, obtained by Kropp[8], to which the latter attributed the structure of the monoether of "*cis*-carane-3,4-diol" by analogy with "*cis*-carane-3,4-diol itself", also has the structure of compound (CVII).[80]

The formation of derivatives of the alcohol (CVIII) was likewise demonstrated in reactions of β-3,4-epoxycarane with sodium acetate in acetic acid[90], by the dehydration of the monotosylate of carane-3β,4β-diol (XXXIe),[91] and by the dehydrohalogenation of ethers of *cis*-3-halogeno-4-hydroxycaranes (XXXIf) under the influence of bases[92,93]:



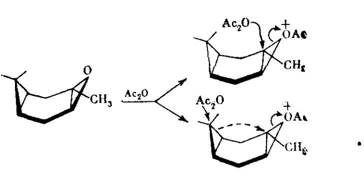
(XXXIe) (XXXIf) .

The acetolysis of compound (XXXIe) with subsequent hydrolysis leads to the diol (CIX),[94] but with an appreciably lower yield than that of the epimeric diol (CIII) in the acetolysis of the monotosylate of carane-3β,4α-diol (XXVIIIe):



(XXXIe) (XXVIIIa) (CIX) .

Comparison of the steric structures of 3,4-disubstituted caranes, the reactions of which are accompanied by a rearrangement with transannular cyclopropyl participation, permits the conclusion that a precondition for the rearrangement is the *cis*-configuration with respect to the relative positions of the cyclopropane ring and the functional groups at the 3-C atom located on the opposite side across the cyclohexane ring. Under the conditions of reactions involving electrophilic addition to β-3,4-epoxycarane, the comparative "activities" of the nucleophilic species attacking the electron-deficient 3-C atom in the intermediate 'onium compound and of the $C_{(1)}-C_{(7)}$ bond in the cyclopropane ring, behaving as an intramolecular nucleophile in the 1,3-transannular shift, are no less important:



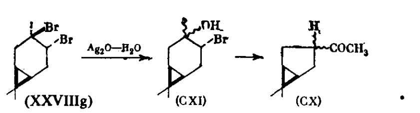
It follows from an examination of the literature data that electrophiles can be arranged in the following sequence in terms of the degree of rearrangement in the reactions of β-3,4-epoxycarane: $Ac_2O > H_2O/H^+ > AcOH/AcONa$.[80,85,86,90]

In the reactions of β-3,4-epoxycarane (VIII) with AcBr in acetic anhydride[92], rearrangements with a 1,3-transannular shift are not observed at all.

3. REARRANGEMENTS WITH CONTRACTION OF THE SIX-MEMBERED RING

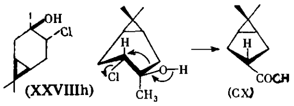
In the last decade studies on the reactions of carane derivatives with substituents at the vicinal secondary and tertiary carbon atoms revealed rearrangements with contraction of the six-membered ring of the Wagner–Meerwein type of rearrangement.

The first data on this rearrangement were obtained by Kuczynski and coworkers[82,83], who showed that, when 3β,4α-dibromocarane (XXVIIIg) is treated with an aqueous suspension of Ag_2O, the main product is 3-acetyl-6,6-dimethylbicyclo[3,1,0]hexane (CX); the configuration at the 3-C atom was not elucidated. The formation of the ketone (CX) from the carane derivative under the conditions of the nucleophilic substitution reaction was explained by the authors on the assumption that there is an intermediate stage involving the conversion of the carane derivative into 4-bromo-3-hydroxycarane (CXI) as an intermediate:



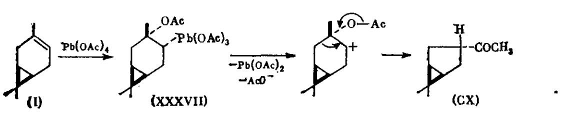
The elimination of HBr from the intermediate is accompanied by a 1,2-shift of the $C_{(2)}-C_{(3)}$ bond in the six-membered ring.

The probability of the involvement of 4-bromo-3-hydroxycarane (CXI) in the conversion of 3β,4α-dibromocarane (XXVIIIg) into the ketone (CX) was confirmed by data obtained in a study of the structures of the stereoisomeric 4-chloro-3-hydroxycarane (XXVIIIh) and 4-bromo-3-hydroxycarane (XXVIIIc). Under these conditions, 4-hydroxy-3-halogenocaranes give a high yield of the ketone (CX):[24,95]

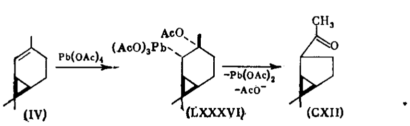


On treatment with silver acetate in acetic acid, 4α-chloro-3β-ethoxycarane forms the ketone (CX) with elimination of a molecule of C_2H_5Cl. 3β,4α-Dichlorocarane (XXVIIIb) is also partly converted into the ketone (CX).[47]

The ketone (CX) has been found in the products of the reaction of 3-carene with $Pb(OAc)_4$.[41,45] It was noted that this reaction may lead to the formation of a *cis*-adduct of the olefin with $Pb(OAc)_4$, the decomposition of which can also involve the contraction of the six-membered ring:

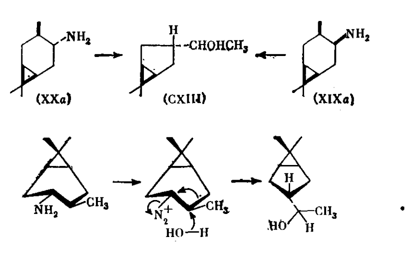


The bicyclic ketone (CXII) is apparently formed similarly in the reaction of 2-carene with $Pb(OAc)_4$:[62]

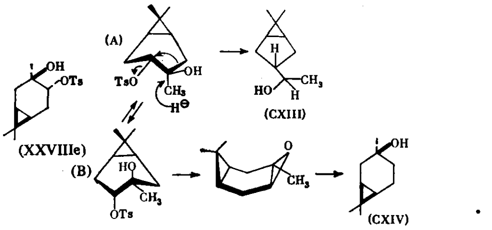


The rearrangement with contraction of the six-membered ring as a result of the 1,2-shift of the $C_{(3)}-C_{(4)}$ bond to the electron-deficient 2-C atom on decomposition of the adduct (LXXXVI) competes with the homoallyl rearrangement in which the cyclopropane ring is involved.

Cocker and coworkers[60] showed that the deamination of the amino-derivatives of *cis*-carane (XIXa) and (XXa), epimeric with respect to the 4-C atom, leads to the formation of appreciable amounts (up to 14% of the mixture of the reaction products) of *trans*-3-(α-hydroxyethyl)-6,6-dimethylbicyclo[3,1,0]hexane (CXIII). The rearrangement can also occur in the diozonium ion as in the case of the 4α-isomer (XXa) and in the carbonium ion with *trans*-attack by the nucleophile relative to the cyclopropane ring:

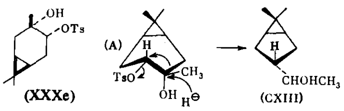


The rearrangement with a 1,2-shift of the $C_{(2)}-C_{(3)}$ bond via a concerted mechanism has been clearly observed in the hydrogenolysis of the monotosylates of carane-3,4-diols. The steric structures of the stereoisomeric carane-3,4-diols (XXVIIIa), (XXXa), and (XXXIa) and possibly of their monoethers consist of equilibrium mixtures of the conformers (A) and (B) with the six-membered ring in the half-chair form[22]. The hydrogenolysis of the monotosylate (XXVIIIe) leads to a 2 : 3 mixture of the two alcohols (CXIII) and (CXIV):

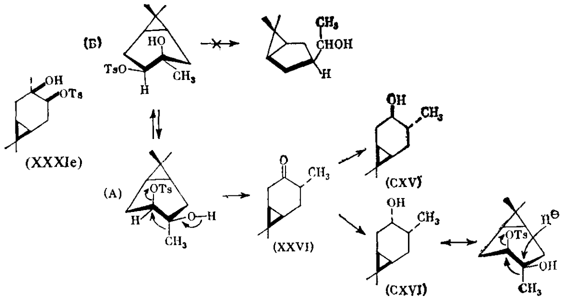


The formation of the former is due to the reaction of the monotosylate (XXVIIIe) in the di-*e*-form (A), since the stereoelectronic requirement imposed on the geometry of the transition state in the rearrangement with ring contraction, namely the anticoplanar disposition of the corresponding bonds, is met in this case. The behaviour of 4α-bromo-3β-hydroxycarane (XXVIIIc) under the same conditions is similar[24].

The hydrogenolysis of the monotosylate (XXXe) proceeds unambiguously with formation of the rearranged alcohol (CXIII); consequently the monotosylate (XXXe) likewise reacts in the preferred conformation (A) having the equatorial $C_{(4)}-O$ linkage:

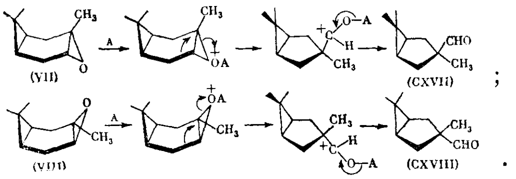


For the monotosylate (XXXIe), conformation (A) with the axial $C_{(4)}-O$ bond is preferred. The rearrangement with contraction of the six-membered ring does not occur here: the processes occurring in the hydrogenolysis by $LiAlH_4$ involve a rearrangement with a 1,2-shift of the $10-CH_3$ group, the stereoelectronic requirement of which (an anticoplanar disposition of the $C_{(4)}$–O and $C_{(3)}$–$C_{(10)}$ bonds)[91] is fulfilled in conformer (A):

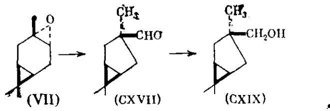


The formation of a 2 : 1 mixture of the epimeric alcohols (CV) and (CVI) as the hydrogenolysis products can be explained if it is assumed that the *E*2 elimination reaction yielding the *trans*-4-caranone (XXVI) takes place under the influence of $LiAlH_4$ together with the hydrogenolysis proper of the monotosylate (XXXIe), leading to *trans*-caran-*trans*-4-ol (CXVI); the stereoselective reduction of the *trans*-4-caranone by $LiAlH_4$ leads preferentially to the alcohol (CXV) with a *cis*-orientation of the OH group relative to the three-membered ring.

It is interesting to note that, among the 3,4-disubstituted carane derivatives, a rearrangement with a different type of contraction of the six-membered ring is characteristic of the stereoisomeric 3,4-epoxycaranes (VII) and (VIII). It involves a 1,2-shift of the $C_{(4)}$–$C_{(5)}$ bond. In 1967, three groups of investigators[97–99] published the results of studies on the isomerisation of 3,4-epoxycaranes under the influence of Lewis acids. The stereoisomeric aldehydes (CXVII) and (CXVIII), the formation of which has been explained by the rearrangement of the carbonium ion intermediates with a 1,2-shift of the ring $C_{(4)}$–$C_{(5)}$ bond, were found among the carbonyl reaction products:



The aldehydes (CXVII) and (CXVIII) are formed from the corresponding stereoisomeric 3,4-epoxycaranes also in the reaction with acetic anhydride[44,86]. According to Teisseire et al.[98], the conversion of 3,4-epoxycaranes into aldehydes is observed under the conditions of gas–liquid chromatography. Silica gel, acting as an electron-accepting agent, also promotes the rearrangement of α,3,4-epoxycarane into the aldehyde (CXVII).[52] On treatment with Al_2O_3, α-3,4-epoxycarane (VII) is partly converted into the alcohol (CXIC), corresponding to the product of the Cannizzaro reaction of the aldehyde (CXVII) formed initially[100]:



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The studies by S. S. Nametkin on terpenes made a most valuable contribution not only to the investigation of this class of natural products but also to organic chemistry as a whole. His brilliant research on camphor homologues enabled him to discover the camphene rearrangement of the second kind or the Nametkin rearrangement (given this name to distinguish it from the camphene rearrangement of the first kind or the Wagner rearrangement). One should mention particularly that Nametkin considered the stereochemical aspect of the complex rearrangements in the reactions investigated, which is a characteristic feature of modern organic chemistry.

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Petroleum Hydrocarbons

P.I.Sanin

The review considers the present state of research on petroleum hydrocarbons and presents the results of studies on the individual hydrocarbons in various fractions of petroleum as well as individual types of petroleum hydrocarbons; in some cases, the possible pathways to the formation of the hydrocarbons are considered. The general characteristics of the distribution of hydrocarbons in petroleum are discussed and certain features of further research on petroleum hydrocarbons are outlined.

The bibliography includes 85 references.

CONTENTS

I. INTRODUCTION

The studies on petroleum hydrocarbons (and other components) are of exceptionally great theoretical importance, since they extend our knowledge concerning the nature and origin of one of the commonest mineral fuels. At the same time the results of such research have been assuming increasing practical importance.

The main raw material for the petroleum processing and petrochemical industries consists of hydrocarbons isolated from petroleum distillates, liquid and gaseous hydrocarbons formed in different thermal and catalytic types of petroleum processing, as well as the hydrocarbons in natural gases. The study of the chemical composition of petroleum—the determination of the nature and structure of hydrocarbons and other petroleum components, the study of the products of the processing of petroleum, the study of natural gases, and the development of new methods for the separation and investigation of complex mixtures of hydrocarbons—is one of the most important fields in petrochemical research. The investigation of the hydrocarbon composition of petroleum is of primary importance also for the development of new methods whereby one can obtain the principal products of the petroleum industry—fuels and lubricating oils, the properties of which are determined in the first place by their chemical composition.

The study of petroleum hydrocarbons has a relatively long history and in our country has always been considered as one of the most interesting fields of chemical science both as regards theory and practice. It is sufficient to point out that research on petroleum hydrocarbons is associated with the names of F.F.Bel'shtein, A.A.Kurbatov, D.I.Mendeleev, A.A.Markovnikov, V.Ogloblin, M.I.Konovalov, N.D.Zelinskii, S.S.Nametkin, B.A.Kazanskii, and others.

Research by foreign scientists has made a significant contribution to our knowledge of petroleum hydrocarbons. Here mention should be made of the systematic investigation of the composition of petroleum based on the programme of the American Petroleum Institute Project 6, carried out from 1928 under Washburn's supervision, from 1935 under Rossini's supervision, and at the present time under Mair's supervision, as well as the research of Waterman, Vlugter, and coworkers (1928–1940), van Nes and van Westen (1950–1959), etc.

The modern period (from 1960) of research on petroleum hydrocarbons is characterised by the application of various physicochemical methods. Techniques for the isolation and separation of hydrocarbons have been improved: different versions of adsorption chromatography, the thermal diffusion method of separation, and methods based on the formation of clathrate compounds—the clathrate method (the use of urea and thiourea), etc. Gas–liquid chromatography, spectroscopic methods, including infrared and ultraviolet absorption spectroscopy, mass-spectrometry, and nuclear magnetic resonance have found very extensive applications in the characterisation and identification of hydrocarbons.

One should note here that progress in the study of petroleum hydrocarbons is to a large extent determined by the development and application of new research techniques. The use of a new, effective method usually leads to a deepening of our knowledge of petroleum hydrocarbons. A striking example is the application of chromatographic methods to the investigation of such hydrocarbons.

Since the present issue of the journal is devoted to the hundredth anniversary of the birthday of the outstanding scientist Sergei Semenovich Nametkin, a separate section of the review describes the fundamental results of the research by Nametkin together with his pupils and coworkers in the field of petroleum hydrocarbons.

Nametkin's Contribution to Research on Petroleum Hydrocarbons

At the beginning of his scientific career, while still a student at Moscow University, Sergei Semenovich Nametkin already wrote his Diploma Thesis "Hydrocarbons in the Caucasus Petroleum, Their Properties and Chemical Reactions" (1902)†. Before entering his chosen

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† Nametkin's work quoted in this section has been published in special collections[1].

field of study, the young scientist surveyed in this report the results of previous investigations of the hydrocarbons in Caucasus petroleum.

The first studies on the Caucasus petroleum, carried out at the time when petroleum processing consisted merely in the preparation of lighting kerosene and fuel mazut, already yielded general ideas about the chemical nature of petroleum. It was established that petroleum includes hydrocarbons of three different series: aromatic hydrocarbons, hydrocarbons of the methane series or paraffins, and other saturated hydrocarbons, which Markovnikov called naphthenes. Nametkin, who already showed his characteristic thoroughness and objectivity in the solution of scientific problems, summarised the results of research on petroleum hydrocarbons, and outlined the problems which required further development. The classical studies by the first investigators of Caucasus petroleum had a strong and fruitful influence on his future career.

In 1907, Nametkin began his research, related to Konovalov's familiar studies, on the interaction of dilute nitric acid with hydrocarbons. These experiments, which were initially undertaken to investigate the hydrocarbons in the Caucasus petroleum, led him to new views on the mechanism of the nitration reaction. The mechanism of the nitrating and oxidising action of nitric acid on saturated hydrocarbons, which Nametkin proposed and justified experimentally, is undoubtedly one of the greatest generalisations in organic chemistry. Nametkin described the fundamental results of this research in his Master's Dissertation (1911). He subsequently used the nitration reaction to investigate petroleum hydrocarbons—paraffin and ceresin.

The range of Nametkin's interest in the field of petroleum chemistry was extremely wide, and in the second half of his career embraced the most important types of research on petroleum chemistry, among which studies on the chemical composition of petroleum occupied an exceptional place. These studies may be conventionally combined in the following groups: methodological problems; investigation of petroleum, petroleum fractions, and natural gases; investigation of certain types of hydrocarbons; the synthesis and study of model petroleum hydrocarbons.

Natural gases from a number of deposits in different regions (Baku, Daghestan, Groznyi, Melitopol, Taman', and Chusov), were investigated for the first time in the Soviet Union on a wide scale under Nametkin's supervision (1931–1933) (together with Zabrodina, Karkanas, Kursanov, Sokolov, and Uspenskii). This systematic research was of interest as regards its methodological aspects and at the same time yielded valuable information about the composition of natural gases, which was also of practical importance. Apart from the main component of the gas (methane), ethane, propane, butane, higher hydrocarbons, and carbon dioxide were determined.

The series of Nametkin's studies was devoted to the investigation of petroleum from new and relatively little investigated deposits in the Soviet Union (1928–1930), Sakhalin petroleums (from the Okha, Nutovo, Katangli, Ekhabi, Chakry, and Lyangri deposits) (together with Putsillo, Shakhnazarova, Abakumovskaya, and Nifontova), Kamchatka petroleum {the Bogachev [tentative transcription] deposit}, and the Urals (Perm) petroleum {the Chusovsko [tentative transcription] settlements}. It is noteworthy that the study of the petroleum from the Chusovsko settlements constituted the first research on petroleums from Second Baku. The petroleum investigated had a high content of sulphur compounds (which reached approximately 5.5%) and in this respect differed sharply from the familiar Caucasus petroleums.

An exceptional growth of production of petroleum from the deposits of Second Baku faced investigators with a new problem—the utilisation of the most effective methods for the processing of sulphur-containing petroleums. Nametkin frequently pointed out that this important problem can be solved only on the basis of a comprehensive study of the chemical composition of sulphur-containing petroleums and their sulphur compounds. The nature of the sulphur compounds in the petroleums from Second Baku was almost unknown.

Nametkin and his coworkers obtained the general characteristics of the first petroleum from Second Baku. Subsequently research was undertaken on the sulphur compounds contained in distillates from certain sulphur-containing petroleums. In the first study, on the kerosene distillate from the Urals petroleum (the Chusovsko settlement deposit), it was already shown that thiophans constitute a considerable proportion of the sulphur compounds of petroleum. This conclusion was reached indirectly, on the basis of the results of the oxidation of sulphur compounds by nitric acid. Subsequent investigations confirmed this conclusion. Thus, hexyl-, heptyl-, and octyl-thiophans were isolated from the light distillates of Ishimbai petroleum (via the corresponding mercury complexes). In addition an aliphatic sulphide (dipropyl sulphide) and mercaptans (butane-2-thiol and pentane-1-thiol) were isolated (together with Sosnina; 1948). Together with Putsillo, Nametkin undertook a systematic study of the proposed methods for the group analysis of sulphur compounds (1943). Tests of the methods, using a wide assortment of synthetic materials comprising individual sulphur compounds, made it possible to establish the limits of the applicability of the individual methods and to outline ways whereby an improved analytical technique for complex mixtures of sulphur compounds could be developed.

Further investigation of the nature of sulphur compounds in petroleum, the development of methods for their isolation from petroleum, and methods for their analysis, which were all problems featuring in Nametkin's research, constitute at the present time one of the most urgent problems in the chemistry of petroleum.

The general research on petroleum convinced Nametkin of the necessity for a more detailed investigation of the chemical composition of the petrol, kerosene, and oil distillates from petroleum. Even an approximate knowledge of the chemical composition of the higher distillates of petroleum is of great significance for the solution of many important theoretical and practical problems. At the same time, investigators in this field encountered the greatest methodological difficulties due to the extreme complexity of the objects of study. On the other hand, it was necessary to refine the existing methods for the determination of the group composition of petroleum distillates, and in many cases to develop new methods. Nametkin's methodological research is in fact associated with this period.

Together with Abakumovskaya (1926–1929), he proposed a new method for the determination of unsaturated compounds in petroleum products—the method of oxygen numbers based on the Prilezhaev reaction (the interaction of benzoyl hydroperoxide and unsaturated hydrocarbons with formation of epoxyalkanes). Together with Robinzon (1928–1938), a method was also developed for the quantitative determination of unsaturated and aromatic hydrocarbons in petrols, which was widely used at the time.

Apart from research on petroleum and the group chemical composition of various petroleum distillates, two other types of research feature in Nametkin's work. The first concerns the isolation of hydrocarbons from petroleum fractions and their identification and the second the synthesis and investigation of the properties of "model" hydrocarbons corresponding to petroleum hydrocarbons as regards their structure and molecular weight. Both these types of research have greatly developed in recent years and are of fundamental importance in the study of the structure of petroleum hydrocarbons.

As an example of the first type of research, one may quote Nametkin's investigations (together with Pokrovskaya and Stepantseva; 1949–1950) on hydrocarbons belonging to the naphthalene series. The picrate method was used; the corresponding petroleum fractions were treated with a solution of picric acid and the resulting alkylnaphthyl picrates were isolated in a pure form after recrystallisation and identified; in some cases, the picrates were decomposed (by steam distillation) and the alkylnaphthalenes isolated were also identified. It was possible to establish in this way the presence of naphthalene, β-methylnaphthalene, and 1,6-dimethylnaphthalene in the middle fractions of the light oil from Surakhany petroleum (the 190–252°C distillate) and of naphthalene, monomethylnaphthalenes, 1,6- and 1,7-dimethylnaphthalenes, trimethylnaphthalenes, and other higher naphthalene homologues in Maikop petroleum (185–265°C and 105–135°C distillates at 2 mmHg). Alkylnaphthalenes constitute 15–20% of all the aromatic hydrocarbons in the middle fractions of the above petroleums. At the same time it was shown that the middle fractions of Emba petroleums (the Dossor and Makat deposits) contain virtually no naphthalene or its homologues. These differences in the content of naphthalene homologues are apparently consistent with the general chemical compositions of the petroleums and are possibly due to their age—the Maikop petroleum deposit belongs to the Tertiary Period and that of Emba petroleums belongs to the Jurassic Period.

Studies on the high-molecular-weight hydrocarbons comprising paraffin and ceresin (together with Nifontova; 1936) should be included in the same group of Nametkin's investigations. They constitute an excellent application of the nitration of saturated hydrocarbons with dilute nitric acid, which had been comprehensively studied by Nametkin in his previous work. It was postulated that it is possible to approach in this way a solution to the problem of the structure of the paraffin and ceresin hydrocarbons, which are difficult to investigate chemically. Nitration under appropriate conditions might lead to the formation of secondary and tertiary nitro-compounds and hence to an experimental solution of the problem of whether or not these hydrocarbons contain tertiary carbon atoms.

It was established that, following the nitration of the hydrocarbons of petroleum paraffin, tertiary nitro-compounds as well as secondary nitro-compounds are formed; the hydrocarbons of petroleum ceresin give rise almost exclusively to tertiary nitro-compounds under the same nitration conditions. Thus it was shown that petroleum paraffins and ceresins contain hydrocarbons with a tertiary carbon atom or, in other words, branched hydrocarbons.

These results constituted a new stage in the understanding of the chemical structure of the hydrocarbons in paraffins and ceresins and stimulated chemists to undertake further research on these complex natural petroleum products. It has now been established that paraffins and ceresins contain, apart from saturated hydrocarbons with normal and branched structures, also high-molecular-weight cyclic hydrocarbons (with long paraffinic chains), this is fully consistent with Nametkin's research—cyclic hydrocarbons in paraffins and ceresin also contain a tertiary carbon atom.

Nametkin's study (together with Pokrovskaya; 1937 to 1938) on the synthesis and properties of hydrocarbons in cyclohexylbenzene and cyclopentylbenzene series as well as other polycyclic hydrocarbons constitutes one of the most important stages in the synthesis of model petroleum hydrocarbons. In terms of their molecular weight, these hydrocarbons serve as models of lubricating oils. The hydrocarbons of the cyclohexylbenzene series were obtained by the condensation of benzene with cyclohexene in the presence of aluminium chloride (the Friedel–Crafts reaction). Cyclohexylbenzene ($C_{12}H_{16}$), 1,4-dicyclohexylbenzene ($C_{18}H_{26}$), 1,3,5-tricyclohexylbenzene ($C_{24}H_{36}$), and, tentatively, 1,2,4,5-tetracyclohexylbenzene ($C_{30}H_{46}$) were obtained in this way. The structures of the hydrocarbons were confirmed by analysis and by the catalytic dehydrogenation of their cyclohexane rings; subsequent hydrogenation led to the reformation of the initial hydrocarbons. The study of the hydrocarbons (their viscosities, solubilities, etc.) led to conclusions about their properties as models of lubricating oils. The hydrocarbons of the cyclopentylbenzene series were investigated and described in the same way: cyclopentylbenzene, two dicyclopentylbenzene isomers, and two tricyclopentylbenzene and tetracyclopentylbenzene isomers.

It is seen from the brief review of his studies on petroleum hydrocarbons that Nametkin developed various branches of this important field in petroleum chemistry. His broad view of the problem and the depth of his research enabled him to obtain results, which in many instances still remain important. On the other hand, the fundamental types of research on petroleum hydrocarbons begun, or suggested, by Nametkin have now been developed by his students and later investigators. In this we see the main importance of Nametkin's work, which constitutes a remarkable stage in the general understanding of petroleum.

A brief outline of the present state of research on petroleum hydrocarbons is given below. The first studies on each type of petroleum usually begin with its general characteristics which are of practical importance. More detailed investigations of petroleum hydrocarbons carried out in different laboratories are in most instances devoted to the solution of individual aspects of the given problem and systematic studies are unfortunately undertaken extremely rarely. Nevertheless, all the more detailed investigations of petroleum can be conventionally divided into three groups: studies on the individual compositions of petroleums and petroleum fractions; studies on specific types of hydrocarbons; determination of the general structures of individual types of hydrocarbons (the modern version of structural-group analysis). Certain general features of the hydrocarbon composition of petroleum have also been outlined as a result of this research.

II. PETROLEUMS FROM NEW DEPOSITS

In the general research on different types of petroleum, investigation of petroleums from newly discovered deposits occupied a significant place. The main aim of the initial study of each petroleum is to obtain its general characteristics, to determine the position of the petroleum in the existing classification of different types, and to establish possible procedures for its processing. In order to characterise the petroleum, one employs established methods and procedures, which in some measure determine the extent to which the petroleum is investigated. At the same time, such characteristics of the petroleum must be consistent with the present development of the petroleum processing and petrochemical industry and must therefore be continuously improved.

There exists at the present time an extended programme of research on petroleums from new deposits. There are also shorter programmes of research on such petroleums. Apart from the usual physicochemical characteristics of petroleum and its fractions, whereby their potential content of commercial products (petrols—aviation and automobile fuels, reactive fuel, kerosene, diesel fuel, raw material for catalytic reforming and catalytic cracking, oil fractions, and bitumen) can be found, provision is made in the extended programme for the determination of the group composition of the fractions, for the determination of straight-chain paraffins in certain fractions by the urea method for the elimination of paraffins (for example the paraffins of the 240–350°C fraction used for the microbiological synthesis of protein), the determination of straight-chain paraffins with the aid of molecular sieves (the fraction boiling up to 200°C), and the determination of the structural-group composition of certain oil fractions.

The results of research on petroleums in the individual Republics and Regions of the Soviet Union are reviewed in monographs and handbooks (see, for example, Refs. 2 to 12).

III. INDIVIDUAL PETROLEUM HYDROCARBONS

Quite naturally, complete determination of individual hydrocarbons can be considered only in relation to light petroleum fractions (petrols). On passing to higher-boiling fractions, the number of possible isomers of individual classes of hydrocarbons becomes so great that the determination of the composition in terms of individual compounds is no longer possible.

Systematic studies over a period of many years on the composition of straight-run petrols in terms of individual compounds were undertaken in 1959 under the supervision of Kazanskii and Landsberg[13]. The combined research technique involved accurate fractionisation, the isolation of aromatic hydrocarbons by adsorption chromatography on silica gel, catalytic dehydrogenation of six-membered naphthenes, and analysis of fractions by Raman spectroscopy. In the course of the investigation, approximately 160 individual hydrocarbons were synthesised and the wavenumbers and the line intensities in the spectra of a large number of individual hydrocarbons were obtained. The combined method made it possible to determine hydrocarbons with boiling points up to 125°C and to find qualitatively, and to some extent quantitatively, the contents of a number of hydrocarbons with boiling points between 125° and 150°C.

It was shown with the aid of the combined method, that the composition of straight-run petrols in terms of individual compounds can be elucidated to the extent of 80 to 90%.[14] In the study of a series of petrols from different types of petroleum, up to 90% of the hydrocarbons was determined—alkanes, cyclopentane and cyclohexane hydrocarbons, and aromatic hydrocarbons. Certain characteristics of the distribution of hydrocarbons in petrol as a function of the type of petroleum were established. Of particular interest is the conclusion that, although petrols derived from different types of petroleum contain approximately the same set of hydrocarbons, their quantitative proportions are extremely different, 10 hydrocarbons present in petrol in greatest amounts constituting about 50% of the petrol from each type of petroleum (Table 1).

One should also note a study[15] of the composition of petrols from Nebit-Dag and Romashkino petroleums in terms of the individual hydrocarbons.

Table 1. Hydrocarbons present in greatest amounts in petrols derived from different types of petroleum.

Surakhany (selected)		Tuimazinsk*		Koschagyl	
hydrocarbon	%	hydrocarbon	%	hydrocarbon	%
Methylcyclohexane	20.05	n-Heptane	9.74	Methylcyclohexane	13.06
Cyclohexane	7.37	n-Hexane	8.43	1,3-Dimethylcyclohexane	6.19
1,3-Dimethylcyclohexane	5.68	n-Octane	7.12	Cyclohexane	4.64
1,2-Dimethylcyclopentane	5.49	n-Pentane	6.32	1,2,4-Trimethylcyclopentane	4.10
Methylcyclopentane	4.59	n-Butane	4.69	2-Methylbutane	3.55
1,2,4-Trimethylcyclopentane	3.45	2-Methylheptane	4.69	Methylcyclopentane	3.51
2-Methylhexane	3.16	Methylcyclohexane	3.74	1,1,3-Trimethylcyclopentane	3.39
1,1-Dimethylcyclohexane	2.99			1,2,3-Trimethylcyclopentane	2.52
Ethylcyclohexane	2.23	2-Methylbutane	3.57	1,2-Dimethylcyclopentane	2.39
1,2,3-Trimethylcyclopentane	2.05	3-Methylhexane	3.43	1,2-Dimethylcyclohexane	2.27
		2-Methylpentane	3.06		
Total	57.06		54.79		45.62

*Tentative transcription (Ed. of Translation).

In the determination of the composition of the light fractions of petroleum in terms of individual compounds, aromatic hydrocarbons are nowadays first separated from alkanes and cyclanes by adsorption chromatography, accurate fractionation, and spectroscopic methods. The advances in the development of chromatographic methods have greatly extended the scope of research and at the same time greatly reduced the time required for the determination of the composition of light petroleum fractions in terms of their individual compounds.

Here one should note the investigation of hydrocarbons in the petrol fractions in the "reference" Ponca (Oklahoma) petroleum carried out in accordance with the programme of the American Petroleum Institute Project 6. This programme led to the determination of the first characteristics of the composition of petrol fractions boiling in the range 40–180°C from seven types of petroleum (Rossini et al.[16], p. 345; Rossini and Mair[17]). The composition of the hydrocarbon fractions was characterised in terms of the individual hydrocarbons of five classes: straight-chain paraffins, branched paraffins, alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes; bicycloparaffins and cycloheptanes were present in extremely low amounts and could be neglected. It was already noted at the time that the petrol fractions from different types of petroleum consist of the same hydrocarbons,[*] differing only in the relative contents of the above five classes; on the other hand, within the limits of each class, the relative amounts of the individual hydrocarbons remain approximately constant and vary within the same limits.

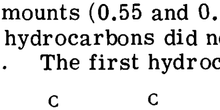
Next a study was made of the 140–180°C distillate from the Ponca petroleum in terms of the individual hydrocarbons, namely branched paraffins and cycloparaffins[18].

The hydrocarbons were isolated by fractionating the distillate (45 litres) on a high-efficiency column using also preparative gas–liquid chromatography; the hydrocarbons were identified by analytical gas–liquid chromatography and by determining the physical as well as spectroscopic characteristics of the hydrocarbons isolated (infrared spectroscopy, NMR, and mass-spectrometry); model hydrocarbons were widely used for identification. 160 fractions, distilling in the range 0.2–0.3°C, were used for the analytical chromatography, which served also for the determination of the quantiative contents of the hydrocarbons. The stationary chromatographic phases were diethylene glycol succinate, silicone nitrile, and *m*-bis-[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene.

As an example of the identification, one may quote 2,4-dimethyloctane[18]. This hydrocarbon was isolated from the fraction boiling at about 156°C and had the refractive index $n_D^{25} = 1.4077$, which is close to the literature value. The mass-spectrometric determination showed that it is a C_{10} paraffin whose molecule contains four methyl groups according to NMR measurements. The results could refer to three hydrocarbons: 2,4-dimethyloctane (b.p. 155.9°C, $n_D^{25} = 1.4069$), 2,2-dimethyloctane (156.9°C and 1.4060), or 1,4-dimethyloctane (157.5°C and 1.4122). The infrared spectrum showed that the hydrocarbon does not contain a tertiary butyl group; the absence of three equivalent methyl groups was likewise confirmed by NMR; thus 2,2-dimethyloctane was excluded. The 4,4-dimethyloctane structure was eliminated by the same type of analysis. At the same time the infrared spectrum showed that the hydrocarbons contain a terminal isopropyl group as well as a butyl group; the structure of the hydrocarbon, corresponding to 2,4-dimethyloctane, was additionally confirmed by the mass spectrum (on the basis of the fragment ions).

Forty-nine paraffins and cycloparaffins, constituting 84% of all possible hydrocarbons in the distillate or 10% in relation to petroleum, were isolated (and identified) from the 140–180°C petroleum distillate, which might contain C_9 and C_{10} hydrocarbons. Six dimethyloctanes of the twelve possible isomers were isolated and identified, namely 2,4-, 2,5-, 2,6-, 3,4-, 4,4-, and 4,5-dimethyloctanes. The remaining six dimethyloctanes, the 2,2-, 2,3-, 2,7-, 3,3-, 3,5-, and 3,6-isomers, are probably present in the petroleum in insignificant amounts only.

It is noteworthy that two paraffins, 2,6-dimethyloctane and 2-methyl-3-propylhexane, were present in petroleum in unusually large amounts (0.55 and 0.64%); the content of each of the other hydrocarbons did not exceed a few hundredths per cent. The first hydrocarbon



$$C{-}\overset{C}{\overset{|}{C}}{-}C{-}C{-}C{-}\overset{C}{\overset{|}{C}}{-}C{-}C$$

can be assigned to isoprenanes—the hydrogenated analogues of acyclic isoprenoids; it was suggested that the second hydrocarbon might have originated from a monocyclic terpene—sylvestrene.

Among the cyclopentanes, 1-methyl-*trans*-2-n-propylcyclopentane, 1-methyl-3-n-propylcyclopentane, and n-butylcyclopentane were identified. Ten of the possible eighteen C_{10} alkylcyclohexanes were also identified. The structural and geometrical isomers of ethylmethylcyclohexane and methylpropylcyclohexane were mainly isolated from C_9 and C_{10} alkylcyclohexanes and identified; also identified were 1-*trans*-2-*cis*-3-trimethyl-, 1-*cis*-2-*trans*-3-trimethyl-, 1,1,2-trimethyl-, and 1,1,3-*cis*-5-tetramethyl-cyclohexanes as well as n-propyl-, isopropyl-, and n-butyl-cyclohexanes.

It is interesting to note that, although the 140–180°C distillate might have contained theoretically a large number of different bicycloparaffins, only nine hydrocarbons belonging to the bicyclo[3,3,0]octane, bicyclo[4,3,0]nonane, bicyclo[3,2,1]octane, and bicyclo[3,3,1]nonane series were isolated and identified:

Judging from the literature data, the hydrocarbon composition of the petrol fractions of petroleum can be found also on the basis of a simplified technique involving only the application of capillary chromatography, the hydrocarbons being identified solely in terms of their retention times without their isolation and characterisation. The saturated hydrocarbons (alkanes and cyclanes) of the 125° to 150°C fraction of the Groznyi petroleum (the Ozek-Suat deposit) were determined in this way[19]. The analysis was carried out using a capillary column equivalent to 60 000 theoretical plates with squalane as the stationary phase. The identification was based on the elution sequence of the hydrocarbons under the chromatographic conditions at 80° and 106°C. The chromatograms of the 125–150°C fraction were interpreted with the aid of a calibration mixture consisting of the products of the isomerisation of n-nonane in the presence of aluminium bromide, which contained a mixture of nonane isomers as well as C_4–C_{10} alkanes (as a result of destructive alkylation). The relative retention times (elution sequence) of the hydrocarbons in the calibration mixture were determined with the aid of model hydrocarbons. After the addition of model hydrocarbons (cyclanes) to the test fraction and the calibration mixture, the cyclanes were identified from the chromatograms. The presence of 61 hydrocarbons (out of the 130 possible compounds), mainly C_9 hydrocarbons, was established in the 125–150°C fraction of the Groznyi petroleum; among the cyclanes, the methyl and ethyl derivatives of cyclopentane and cyclohexane were widely represented.

It is noteworthy that the chromatographic method for the determination of hydrocarbons described above is relatively rapid and is widely used; however, apart from the fact that one cannot characterise hydrocarbons by this procedure (they are not isolated), there are limitations associated with the poor chromatographic separation of certain types of hydrocarbons. Thus the chromatographic peaks of monosubstituted nonane isomers overlap the peaks of cyclopentane hydrocarbons. The six geometrical isomers of 1,2,3,4-tetramethylcyclopentane are also not separated by the chromatographic method.

The research on the hydrocarbons in the petrol fractions of petroleum is related to the research on the hydrocarbons from the gas-condensate deposits. Here mention should be made primarily of extensive systematic investigations of the gas condensates from Central Asian deposits—in Turkmenistan and Uzbekistan[20–23]. A large proportion of the gas deposits which have been prospected and brought into production in recent years are known to be of the gas-condensate type; the gases from these deposits contain 2–5% and more of liquid hydrocarbons. In view of the enormous production of natural gas, amounting to hundreds of thousand millions of cubic metres, liquid hydrocarbons (condensates) are a valuable and readily available raw material for chemical processing. In the study quoted above[19], it was shown that the hydrocarbon composition of the 125–150°C fraction of the condensate from the Shur-Tepe deposit (Turkmenistan) is close to that of the similar fraction of the Groznyi petroleum (the Ozek-Suat deposit).

The bulk of the condensates from all the gas-condensate deposits in Central Asia investigated (50 different condensates have been studied) consist of ligroin fractions (100–200°C) or C_7-C_{13} hydrocarbons; the content of the lightest fraction in the condensate (boiling up to 100°C) rarely exceeds 10%. Certain condensates are distinguished by a high content of benzene homologues (20–30% and more) and cyclohexane homologues (up to 20–25%); on the other hand, another group of condensates have a low content of these hydrocarbons and a high content of cyclopentane homologues.

Certain general characteristics of the hydrocarbon composition of the condensates may be noted. Among branched paraffins, the monomethyl derivatives predominate, namely 2-, 3-, and 4-methyl-alkanes, the substances present in largest amounts being 2-methylalkanes, namely 2-methylpentane, 2-methylhexane, and 2-methylheptane. The dimethylalkanes contain mainly 2,3- and 2,4-dimethylalkanes. Apart from cyclopentane itself, the cyclopentane hydrocarbons consist mainly of methyl- and ethyl-cyclopentanes as well as 1,2- and 1,3-dimethylcyclopentanes. The condensates usually contain all three dimethylcyclohexane isomers (1,2- 1,3-, and 1,4-), the proportion of 1,3-dimethylcyclohexane ranging from 50 to 70% of the total content of all three isomers. It is of interest that the same proportions have been observed for dimethylbenzenes, the 1,3-isomer (*m*-xylene) predominating. One may also note that toluene and 1,2,4-trimethylbenzene predominates in the condensate.

One can now assume that the determination of the composition of the light petroleum fractions (boiling up to about 150°C) in terms of the individual hydrocarbons presents no difficulties. The study of such composition of the middle petroleum distillates has naturally been carried out on a smaller scale. As an example, one may quote the results of the investigations of the Romashkino[24] and Arlansk[25] petroleums. Both types of petroleum have a high content of sulphur compounds (containing 1.8 and 2.84% of sulphur) and tars (9.9 and 20.3%); they can be classified as paraffinic petroleums (their paraffin contents are 4.9 and 4.7%). The petroleums were investigated on the basis of a single programme. Their general characteristics and information about their composition in terms of individual hydrocarbons were obtained. After deasphalting at a low temperature, the petroleum was distilled with isolation of the 180–350°C fraction (the kerosine–gas oil distillate), which was then investigated further. The distillate contained about 19% of straight-chain paraffins and 20% of aromatic hydrocarbons. Various methods for the separation and identification of the hydrocarbons were used in the course of the investigation: clear-cut fractionation, complex formation with urea, adsorption chromatography, gas–liquid chromatography, spectroscopic methods, and catalytic dehydrogenation.

The 180–200°C, 200–300°C, and 300–350°C fractions of the distillate were separated into two components by adsorption chromatography on silica gel: a mixture of paraffins and cycloparaffins and a mixture of aromatic hydrocarbons and sulphur compounds. The straight-chain paraffins were isolated from the mixture of paraffins and cycloparaffins by complex formation with urea and then identified in the usual way by gas–liquid chromatography. It is noteworthy that the hydrocarbons isolated with urea contained, apart from straight-chain paraffins, a certain amount of branched paraffins and cycloparaffins. For example, it has been established that the hydrocarbons crystallising from the 300–350°C fraction of the Romashkino petroleum and forming a complex with thiourea contained 60% of straight-chain paraffins and approximately 40% of branched paraffins and alkylcycloparaffins. Another method for the isolation of straight-chain paraffins from the mixture of saturated hydrocarbons by adsorption chromatography on activated charcoal was developed in the course of the investigation. Subsequently this method was improved and used to separate naphthenes and branched paraffins—the mixture of petroleum hydrocarbons which is most difficult to separate[26].

The list of straight-chain paraffins contained in the 180–350°C distillate is given below. The boiling points of the hydrocarbons, based on the literature data, make it possible to infer the range corresponding to their ebullition.

Straight-chain paraffins

		B.p., °C
$C_{11}H_{24}$	undecane	195.8
$C_{12}H_{26}$	dodecane	216.3
$C_{13}H_{28}$	tridecane	235.5
$C_{14}H_{30}$	tetradecane	253.6
$C_{15}H_{32}$	pentadecane	270.6
$C_{16}H_{34}$	hexadecane	287.1
$C_{17}H_{36}$	heptadecane	302.7
$C_{18}H_{38}$	octadecane	317.5
$C_{19}H_{40}$	nonadecane	331.7
$C_{20}H_{42}$	eicosane	345.3

Thus the distillate contains all ten possible straight-chain paraffins; the content of each hydrocarbon is about 0.4–0.5% in both Romashkino and Arlansk petroleums.

As mentioned above[24,25], the aromatic hydrocarbons isolated by adsorption chromatography contain an appreciable amount of organosulphur compounds; these were oxidised by hydrogen peroxide in glacial acetic acid to sulphoxides, and the latter were separated from aromatic hydrocarbons by adsorption chromatography on silica gel. The purified aromatic hydrocarbons were separated by adsorption chromatography on alumina gel into aromatic hydrocarbons containing one and two benzene rings. The content of aromatic hydrocarbons in the initial distillate was approximately 20% and most of them (80–90%) consisted of alkylbenzenes. The hydrocarbons were distilled with isolation of narrow fractions (2° and 5°C fractions). They were identified by gas–liquid chromatography and infrared and ultraviolet spectroscopy. Model hydrocarbons were used for comparison.

Twenty benzene homologues, mainly with the composition $C_{10}H_{14}$ and $C_{11}H_{16}$, were determined on the basis of the boiling points of the corresponding 170–215°C fractions:

Benzene homologues in petroleum (b.p.170–215°C)

		B.p., °C
C_9H_{12}	1,2,4-trimethylbenzene	169.35
$C_{10}H_{14}$	s-butylbenzene	173.30
$C_{10}H_{14}$	4-isopropyl-1-methylbenzene	177.25
$C_{10}H_{14}$	1-methyl-3-n-propylbenzene	181.75
$C_{10}H_{14}$	n-butylbenzene	183.85
$C_{10}H_{14}$	1-methyl-2-n-propylbenzene	184.75
$C_{10}H_{14}$	2-ethyl-1,4-dimethylbenzene	186.45
$C_{10}H_{14}$	4-ethyl-1,3-dimethylbenzene	188.45
$C_{10}H_{14}$	2-ethyl-1,3-dimethylbenzene	189.95
$C_{10}H_{14}$	3-ethyl-1,2-dimethylbenzene	193.80
$C_{10}H_{14}$	1,2,4,5-tetramethylbenzene	196.85
$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene	198.15
$C_{10}H_{14}$	1,2,3,4-tetramethylbenzene	205.10
$C_{11}H_{16}$	3-phenylpentane	191.0
$C_{11}H_{16}$	4-s-butyl-1-methylbenzene	192.8
$C_{11}H_{16}$	2-phenylpentane	193.0
$C_{11}H_{16}$	3-n-butyl-1-methylbenzene	205.0
$C_{11}H_{16}$	n-pentylbenzene	205.3
$C_{12}H_{18}$	1,4-di-isopropylbenzene	210.4
$C_{12}H_{18}$	4-s-butyl-1,2-dimethylbenzene	215.1

It is seen from the above list that only a small proportion of the hydrocarbons which may be present in the distillate were determined. This is because the difficulty of identifying the hydrocarbons increases with increase of their molecular weights and boiling points. It is also well known that the determination of hydrocarbons in petroleum depends directly on the availability of model hydrocarbons, the synthesis of which also becomes more complicated with increase of the molecular weight of the hydrocarbon.

The high content of tetramethylbenzene isomers in petroleum is striking. Whereas the content of each hydrocarbon [of each of the other hydrocarbons?] does not exceed 0.02–0.04%, the contents of 1,2,4,5-, 1,2,3,5-, and 1,2,3,4-tetramethylbenzenes were found to be 0.064, 0.13, and 0.22%. It is interesting to note that high contents of tetramethylbenzenes for the same proportions of the isomers were found by American investigators in the petroleum from the Ponca deposit[17].

As will be shown below, aromatic hydrocarbons with methyl groups in general predominate among the aromatic hydrocarbons in petroleum. Twenty hydrocarbons boiling in the range 215–300°C have been determined in the fractions containing hydrocarbons with two benzene rings. They consist mainly of naphthalene homologues:

Hydrocarbons with two benzene rings
(b.p. 215-300°C)

		B.p., °C
$C_{10}H_8$	naphthalene	217.96
$C_{11}H_{10}$	2-methylnaphthalene	241.05
$C_{11}H_{10}$	1-methylnaphthalene	244.64
$C_{12}H_{10}$	biphenyl	254.9
$C_{12}H_{12}$	2-ethylnaphthalene	257.9
$C_{12}H_{12}$	1-ethylnaphthalene	258.7
$C_{12}H_{12}$	2,6-dimethylnaphthalene	262.0
$C_{12}H_{12}$	2,7-dimethylnaphthalene	262.3
$C_{12}H_{12}$	1,7-dimethylnaphthalene	263.0
$C_{12}H_{12}$	1,6-dimethylnaphthalene	264.0
$C_{12}H_{12}$	1,3-dimethylnaphthalene	265.0
$C_{12}H_{12}$	1,5-dimethylnaphthalene	265.0
$C_{12}H_{12}$	1,2-dimethylnaphthalene	266.0
$C_{12}H_{12}$	2,3-dimethylnaphthalene	268.0
$C_{12}H_{12}$	1,4-dimethylnaphthalene	130 (12 mmHg) . *cm.*)
$C_{12}H_{12}$	1,2-dimethylnaphthalene	268.5
$C_{12}H_{12}$	1,5-dimethylnaphthalene	269.1
$C_{13}H_{14}$	1-propylnaphthalene	272.0
$C_{13}H_{14}$	2-propylnaphthalene	273.5
$C_{14}H_{16}$	2-s-butylnaphthalene	274—276
$C_{12}H_{10}$	acenaphthene	277.3
$C_{14}H_{14}$	1,2-diphenylethane	284.7
$C_{13}H_{14}$	2,3,6-trimethylnaphthalene	286.0
$C_{13}H_{10}$	fluorene	297.2

Each hydrocarbon of this series was present in the petroleum in an amount corresponding to several thousandths per cent. There were high contents of naphthalene (0.014%), 1-methyl- and 2-methyl-naphthalenes (0.023 and 0.029%) and certain dimethylnaphthalenes.

Of the ten possible dimethylnaphthalene isomers, nine were found in the petroleum, the missing isomer being 1,8-dimethylnaphthalene. The bulk of the dimethylnaphthalenes (70–80% of the total naphthalenes) consisted of four isomers: 1,6-, 2,6-, 2,7-, and 1,7-dimethylnaphthalenes. It is remarkable that the quantitative proportions of the isomers are very similar in a wide variety of petroleums.

Table 2 presents as an example data for two types of petroleum.

It is interesting that the quantitative proportions of the dimethyldecalins found in the petroleums are close to the proportions obtained after prolonged disproportionation of dimethyldecalin isomers on an aluminosilicate catalyst at 450°C.[27] The similarity of the compositions of the dimethylnaphthalenes from different types of petroleum demonstrate yet again the common features in the composition of petroleum hydrocarbons in general.

Apart from naphthalene homologues, biphenyl, 1,2-diphenylethane, acenaphthene, and fluorene were detected in the petroleum. A number of decalin homologues were also determined. For this purpose, the fractions of naphthenoparaffinic hydrocarbons were dehydrogenated in the liquid phase in the presence of an iron-platinum catalyst after the elimination of straight-chain paraffins[28]. The resulting naphthalene homologues were isolated and identified as described above. Many decalin homologues were determined by this indirect procedure in the 200° to 300°C distillate; their structures corresponded to those of the naphthalene homologues determined previously in the petroleum: 2-methyl- and 1-methyl-decalins, 2-ethyldecalin, and all the isomeric dimethyldecalins except 1,8-dimethyldecalin. Using the dehydrogenation reaction, hydrocarbons with mixed structures were also found in the petroleum: cyclohexylbenzene and 1-cyclohexyl-2-phenylethane.

Table 2. The comparative contents of dimethylnaphthalene isomers in different types of petroleum.

Hydrocarbon	Contents of dimethylnaphthalene isomers, wt.% (relative to total content of dimethylnaphthalenes	
	Arlansk petroleum	American petroleum (Ponca)
2,6-Dimethylnaphthalene	17.2	19.4
2,7-Dimethylnaphthalene	13.4	14.4
1,7-Dimethylnaphthalene	14.6	21.2
1,6-Dimethylnaphthalene	27.2	28.2
1,3-Dimethylnaphthalene	7.2	0.2
2,3-Dimethylnaphthalene	5.9	7.2
1;4-Dimethylnaphthalene	4.6	2.8
1,5-Dimethylnaphthalene	2.9	3.7
1,2-Dimethylnaphthalene	7.0	2.4
1,8-Dimethylnaphthalene	nil	nil

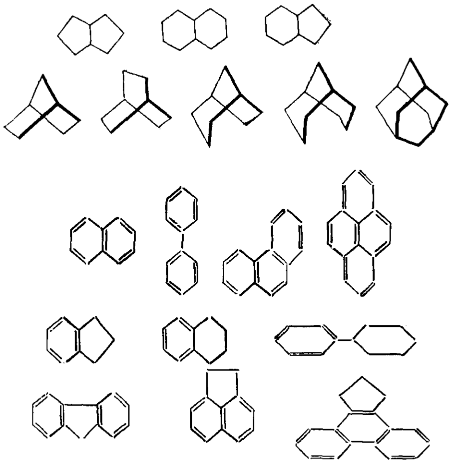
Summarising the results of studies on the composition of petroleum hydrocarbons in terms of individual compounds, we see that more than 600 hydrocarbons have now been isolated from petroleum or determined in petroleum. Different classes of hydrocarbons have been investigated to different extents. Paraffinic hydrocarbons with straight-chain structures have been studied most thoroughly. This is understandable, since straight-chain paraffins do not have isomers. Their isolation from petroleum fractions (adsorption chromatography, the formation of a complex with urea, isolation with the aid of zeolites—molecular sieves) and identification (gas–liquid chromatography) do not present difficulties at present, as already mentioned above. Preliminary detailed investigations of the physicochemical properties of straight-chain paraffins, particularly their tendency to form solid solutions, have proved of much assistance in their identification[29].

The presence of all straight-chain paraffins from n-butane (b.p. −0.5°C) to n-tritriacontane $C_{33}H_{68}$ (b.p. 475°C) in petroleum has been demonstrated; some of the straight-chain paraffins have been isolated in a pure form with a purity exceeding 99 mole %. The content of straight-chain paraffins in petroleum decreases with increase of their molecular weight; that of the highest straight-chain paraffins is 0.1% or less[30].

It is of interest that, in the solution of the problem of the microbiological synthesis of protein from the paraffinic hydrocarbon of petroleum, the past studies on hydrocarbons of this series made it possible to solve over a short period methodological problems associated with the determination of the paraffins (and to some extent aromatic hydrocarbons) in the initial fractions used for the synthesis and in the biological products obtained.

The list of the hydrocarbons detected in petroleum shows how limited is our knowledge of the hydrocarbons in the middle fractions of petroleum, particularly of branched paraffins and cyclanes as well as hydrocarbons with mixed structures containing benzene and cycloparaffin rings. Only a few of the hydrocarbons detected in petroleum boil above 200°C.

The structural formulae of the principal types of cyclanes and aromatic hydrocarbons containing two and more rings, which have been detected in the middle fractions of petroleum, are listed below:



Certain homologues of these hydrocarbons and their isomers have been found.

It is of interest to compare the results of the study of the hydrocarbon composition of petroleum obtained in the reserach laboratories of the Soviet Union and abroad, in the first place those of the American Petroleum Institute Project 6.[16,18,30–34] The total numbers of hydrocarbons determined are approximately the same, but the alkyl derivatives of cyclopentane and bicyclanes have been studied more fully in the Soviet Union. Foreign investigators have paid more attention in recent years to the isolation and determination of aromatic petroleum hydrocarbons. It is noteworthy that nowadays investigators endeavour in most cases to determine the hydrocarbon chromatographically without isolating it from petroleum. Because of this, the properties of certain hydrocarbons detected in petroleum have sometimes not been investigated.

The enormous number of structural and geometrical isomers in the middle fractions of petroleum limits the possibility of their determination. Other research techniques described below are of considerable importance in this field.

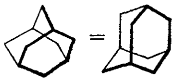
IV. INDIVIDUAL TYPES OF HYDROCARBONS

We may note one group of hydrocarbons in the middle fractions of petroleum, namely methylnaphthalenes, the composition of which in terms of individual compounds was investigated within certain limits as early as the 1950s. Naphthalene homologues form crystalline picrates (molecular compounds) by reaction with picric acid and for this reason they were isolated from petroleum fractions relatively long ago. The modern methods for their identification were described above.

Four types of hydrocarbons, namely alkyl derivatives of adamantane and hydrocarbons which are the hydrogenated analogues of terpenes (isoprenanes, steranes, and triterpanes), have been actively investigated recently.

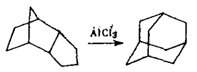
(a) Adamantane and Its Homologues

Adamantane or tricyclo[3,3,1,$1^{3,7}$]decane, which has a very unusual polyhedral structure, has been isolated from Godonin petroleum (Czechoslovakia) and has been investigated by Landa and Machacek[35] in 1933. It is a crystalline substance with a melting point of 269°C (the highest among the known hydrocarbons). The adamantane molecule consists of three condensed cyclohexane rings in the chair form; the steric dispositions of the carbon atoms in the adamantane molecule forming, as it were, a cage closed on all sides, is the same as in the crystal structure of diamond—hence its name:

 .

Mention should be made of yet another factor—the discovery in petroleum of this hydrocarbon with its remarkable structure and properties initiated the development of an extremely important field in modern organic chemistry—the chemistry of adamantane. Adamantane derivatives have now found a wide variety of applications (as medicinal substances, polymers, etc.).

Adamantane is usually obtained by the isomerisation of the fully hydrogenated cyclopentadiene dimer (*endo*-trimethylenenorbornane) in the presence of aluminium chloride[36]:

 .

The isomerisation takes place also over the aluminosilicate catalyst[37]. We are unable to consider here the reaction mechanism, which is discussed by Schleyer and Donaldson[38].

The adamantane content in the middle fractions of Soviet petroleums has been determined by the method of Landa and Hala[39]. The entire distillate which may contain adamantane is obtained from petroleum by steam distillation; adamantane is concentrated by repeated complex formation with thiourea and is isolated by preparative gas–liquid chromatography. The adamantane contents in various Soviet petroleums, even those with a high content of cyclanes such as the petroleums from the Balakhansk [tentative transcription] and Surakhany deposits, are small and usually amount to 0.004–0.01%.[39] Petroleum from the Ponca deposit (USA) was found to contain 0.004% of adamantane[40]. The content of adamantane is somewhat higher in the petroleum from the Godonin deposit, where it was first discovered[41].

The presence of a number of alkyladamantanes in petroleum has now been established. They can be isolated and identified as follows. The petroleum fraction consisting of branched paraffins and cyclanes is separated by thermal diffusion, which yields a concentrate of tricyclic hydrocarbons containing alkyladamantanes. The efficiency of the thermal diffusion method in this case has been confirmed with the aid of artificial mixtures of synthetic hydrocarbons. The concentrate, containing a considerable amount of "non-adamantane" structures in addition to the alkyladamantanes, is subjected to catalytic cracking and dehydrogenation under pulsed conditions over a platinum catalyst (0.5%) on alumina at 420°C and the resulting unsaturated and aromatic hydrocarbons (formed by the dehydrogenation of the cyclanes containing the cyclohexane ring) are removed by adsorption chromatography on activated silica gel. Under the conditions described, alkyladamantanes, which are very stable, are hardly altered. Only partial epimerisation is observed, for example, there is partial conversion of *cis*-1,4-dimethyladamantane into *trans*-1,4-dimethyladamantane[43]. The alkyladamantanes in the concentrate are then identified by capillary gas–liquid chromatography (with squalene as the stationary phase)[42,43].

The 200–250°C fraction of heavy Balakhansk petroleum (Baku), which might have contained methyl- and ethyladamantanes, was investigated in this way. The yield of the 200–225°C fraction was 2.8% and its content of the mixture of branched paraffins and cyclanes was 85%. A concentrate of tricyclanes was isolated from the mixture and a concentrate of alkyladamantanes was obtained.

Twenty-four $C_{11}-C_{14}$ alkyladamantanes with methyl and ethyl substituents were identified. The total content of alkyladamantanes was 0.02%, which is ten times more than the content of adamantane itself in this petroleum (0.001%).

The presence of mono-, di-, tri-, and tetra-substituted alkyladamantanes, containing methyl and ethyl substituents in various positions in the adamantane ring, has now been established in different types of petroleum[42-46].

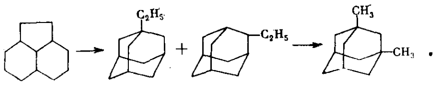
Petroleum alkyladamantanes
(The alkyl groups and their positions in the adamantane nucleus are indicated)

C_{11}	C_{13}	C_{14}
1-methyl-	1,3,5-trimethyl-	1,3,5,7-tetramethyl-
2-methyl-	1,3,6-trimethyl-	1,3,5,6-tetramethyl-
	1,3,4-trimethyl	1-ethyl-2,5-dimethyl-
	1-ethyl-3-methyl-	1,2,3,5-tetramethyl-
C_{12}	4-ethyl-1-methyl-	
	1,2,6-trimethyl-	
1,3-dimethyl-	1,2,4-trimethyl-	
1,4-dimethyl-		
1,2-dimethyl-		
1-ethyl-		
2-ethyl-		
2,2-dimethyl-		
2,4-dimethyl-		

It is remarkable that, together with the most stable alkyladamantanes having substituents at the tertiary bridgehead carbon atoms in the adamantane nucleus (in the 1-, 3-, 5-, and 7-positions), alkyladamantanes with substituents at secondary carbon atoms (in the 2-, 4-, and 6-positions) have been detected in petroleum in considerable amounts. Consequently, the proportions of the alkyladamantane isomers in different types of petroleum do not correspond to equilibrium.

Compounds containing the adamantane nucleus have not been detected among substances of plant and animal origin. One must therefore suppose that the hydrocarbons of the adamantane series have been formed as a result of secondary processes—for example as a result of the isomerisation of other tricyclic hydrocarbons present in petroleum.

Tricyclic (perhydroaromatic) hydrocarbons, namely perhydroacenaphthene (C_{12}), perhydrofluorene (C_{13}), and perhydroanthracene (C_{14}), are known to isomerise to alkyladamantanes in the presence of $AlBr_3$.[47] The mechanism of the process involving perhydroacenaphthene is as follows:



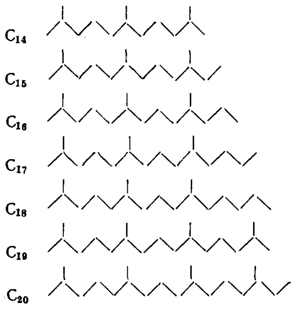
The isomerisation takes place also under the influence of other metal halides[44] and the corresponding bicyclic hydrocarbons are likewise capable of isomerising adamantanes[48].

Tricyclic hydrocarbons undergo an analogous transformation also under the conditions of heterogeneous catalysis over an aluminosilicate catalyst or alumina at moderate (between approximately 180 and 250°C) and higher temperatures[48-51]. The alkyladamantanes formed in the reaction then undergo further isomerisation, there is an increase in the total number of substituents, a decrease in the length of the substituents, and preferential formation of the most stable alkyladamantanes containing methyl or other groups only at the bridgehead positions of the adamantane nucleus.

As already mentioned above, in the series of alkyladamantane isomers with the same molecular weight the proportions of petroleum adamantanes are far from the equilibrium values. Thus the contents of 1,3,5-, 1,3,6-, and 1,3,4-trimethyladamantanes in petroleum were (relative to the sum of C_{13} alkyladamantanes) 21.5, 14, and 28.5%, while the contents in the equilibrium mixture (obtained by isomerisation over alumina) were 92.5, 3, and 3% respectively. At the same time, there is a fairly satisfactory correspondence between the relative contents of petroleum alkyladamantanes and their contents in the non-equilibrium mixtures obtained in the catalytic isomerisation of tricyclanes. Thus, even if alkyladamantanes were formed from tricyclanes, this must have occurred under conditions preventing the completion of the isomerisation reaction with formation of stable isomers alone; kinetic factors may have played a significant role in this process.

(b) Petroleum Isoprenanes

Alkanes with the isoprenoid structure were discovered in petroleum in the 1960s. Aliphatic polyperterpenes, having a polyisoprene skeleton with a characteristic alternation of methyl chain substituents at intervals corresponding to three methylene groups, which may be regarded as isoprene polymerisation products, are classified as aliphatic isoprenoids in organic chemistry. The term "isoprenoid petroleum hydrocarbons" has been very arbitrarily attributed to saturated branched alkanes, which are hydrogenated analogues of isoprenoids. The present author believes that the above hydrocarbons should be called isoprenanes, by analogy with terpanes (hydrogenated analogues of terpenes) and steranes (hydrogenated analogues of steroids). The structures of $C_{14}-C_{20}$ isoprenanes can be represented as follows:

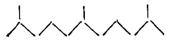


Mainly 2,6-dimethylalkanes, 2,6,10-trimethylalkanes, and 2,6,10,14-tetramethylalkanes are assigned to hydrocarbons of this type.

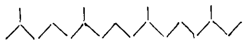
The syntheses of the majority of isoprenane hydrocarbons as models of petroleum hydrocarbons have now been described[52,53]. Thus 2,6-dimethylalkanes ($C_{10}-C_{13}$) can be obtained from acyclic terpenoids—citronellol, citral, pseudoionone; 2,6,10-trimethylalkanes ($C_{14}-C_{18}$) can also be obtained from pseudoionone. In a general form, the synthesis of alkanes of this type can be carried out via the following scheme:

corresponding ketone → alcohol → unsaturated hydrocarbon → alkane.

For example the alcohol 2,6,10-trimethylundeca-2,6-diene-10-ol has been obtained by the Grignard reaction from geranylacetone, synthesised by the condensation of linalool and ethyl acetoacetate; the alcohol was then dehydrated to the corresponding triene and the hydrogenation of the latter yielded 2,6,10-trimethylundecene:



Phytane (2,6,10,14-tetramethylhexadecane) can be obtained by the dehydration of isophytol (2,6,10,14-tetramethylhexadec-15-en-14-ol) and subsequent reduction of the resulting tetramethylhexadiene to tetramethylhexadecane:

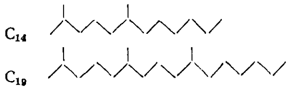


The physicochemical characteristics of the isoprenanes synthesised are listed in Table 3.

Table 3. Physicochemical characteristics of isoprenanes.

Hydrocarbon	B.p., °C (mmHg)	B.p., °C (at 760 mmHg; recalc.)	Solidification temp., °C	n_D^{20}	ρ_4^{20}
2,6,10-Trimethylundecane	103.2—103.8 (11)	236.2—237.5	<—100	1.4270	0.7593
2,6,10-Trimethyldodecane (farmesane)	118.0 (10)	253	<—90	1.4335	0.7714
2,6,10-Trimethyltridecane	123.5 (9)	272	<—90	1.4349	0.7773
2,6,10-Trimethyltetradecane	127.5 (7)	285	<—80	1.4361	0.7806
2,6,10-Trimethylpentadecane	140.3 (8)	300	<—70	1.4400	0.7845
2,6,10,14-Tetramethylpentadecane (pristane)	146—147 (4)	331.2—332.5	<—70	1.4390	0.7845
2,6,10,14-Tetramethylhexadecane (phytane)	139.7—140.2 (3)	352.5—353.0	—70	1.4420	0.7935

Branched alkanes, whose molecules contain only fragments of the isoprenane (polyisoprene) structure have also been synthesised, for example, 2,6-dimethyldodecane, 2,6,10-trimethylhexadecane, etc.[54]:



The isoprenanes pristane and phytane were first detected in Iranian[55] and Western Texas[56,57] petroleums. It has now been established that all petroleums contain some isoprenanes; they have also been detected in shale, bituminous coal, and various bituminous sedimentary rocks[58,59]; their formation is apparently associated with a plant substance (phytol), which has a definite bearing on the problem of the origin of petroleum and caustobioliths in general. The wide occurrence of these unusual hydrocarbons and their biogenic origin ("biological labels") has attracted the attention of investigators.

Various methods, particularly capillary gas chromatography and mass spectrometry, are used to determine isoprenanes. Two approaches to the identification of isoprenanes in petroleum have been devised; the first provides for a preliminary preparation in one way or another of isoprenane concentrates from fairly narrow fractions and their subsequent analysis and the second involves direct determination of isoprenanes in broad fractions with the aid of analytical gas chromatography.

A scheme has been described for the investigation of hydrocarbons of the type of isoprenanes in 180–350°C petroleum fractions, which involves the elimination of aromatic hydrocarbons (adsorption on silica gel) and straight-chain alkanes (complex formation with urea) from the fraction, separation of branched alkanes and cyclanes by adsorption chromatography on activated charcoal, and their vacuum distillation[60]. The development of a method for the separation of branched alkanes and cyclanes presented the greatest difficulties—separation of this kind is still an urgent problem and in this connection we may mention, together with the use of activated charcoal as an adsorbent, the work by American investigators in which Sephadex has been used as the adsorbent[61]. Branched alkane fractions, in which isoprenanes were determined by capillary chromatography and mass-spectrometry, were thus obtained. A mass-spectrometric method has been developed for the quantitative determination of isoprenanes in petroleum[62]. The entire study has been carried out using model hydrocarbons.

Isoprenanes can be determined also by methodologically simpler methods. The 150–350°C broad petroleum fraction, containing the main bulk of petroleum isoprenanes (with the $C_{11}-C_{20}$ composition), was directly analysed for isoprenanes by capillary gas chromatography (with Apiezon L as the stationary phase) after preliminary elimination of aromatic hydrocarbons by adsorption on silica gel[53]. The contents of isoprenanes in various types of petroleum[57,60] are listed in Table 4.

Table 4. The contents of isoprenanes in different types of petroleum (wt.%).

Hydrocarbon	Composition	B.p., °C	Petroleum		
			Romashkino	Irkutsk	Western Texas
2,6,10-Trimethylundecane	C_{14}	236.2—237.5	0.2	0.20	0.10
2,6,10-Trimethyldodecane (farmesane)	C_{15}	253	0.2	0.20	0.20
2,6,10-Trimethyltridecane	C_{16}	272	0.2	0.15	0.20
2,6,10-Trimethyltetradecane	C_{17}	285	0.1	0.10	not found
2,6,10-Trimethylpentadecane	C_{18}	300	0.2	0.30	0.06
2,6,10,14-Tetramethylpentadecane (pristane)	C_{19}	331.2—332.5	0.2	0.30	0.50
2,6,10,14-Tetramethylhexadecane (phytane)	C_{20}	352.5—353	0.4	0.50	0.20

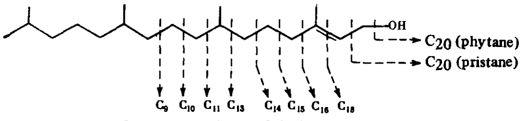
The Table shows that petroleums contain all seven $C_{14}-C_{20}$ isoprenanes (2,6,10-trimethyl- and 2,6,10,14-tetramethyl-alkanes). Their overall content in petroleum is approximately 1.5–2.0% and the amount of each hydrocarbon is approximately 0.2–0.3%. Certain types of petroleum have enhanced contents of pristane (C_{19}) and phytane (C_{20}).

The contents of isoprenane hydrocarbons in four Soviet paraffinic petroleums {Ronashkino, Groznyi, Surgut

(Western Siberia), and Usinsk [tentative transcription] (Ukhta)} have been determined[53], and, apart from the $C_{14}-C_{20}$ hydrocarbons mentioned above, $C_{11}-C_{13}$ dimethylalkanes were found, namely 2,6-dimethylnonane, 2,6-dimethyldecane, and 2,6-dimethylundecane. The overall content of ten $C_{11}-C_{20}$ isoprenane hydrocarbons (2,6-dimethyl-, 2,6,10-trimethyl-, and 2,6,10,14-tetramethylalkanes) was 2–3%.

Thus the petroleums are distinguished by a high content of isoprenanes, the main bulk of which (30–40%) consists of pristane and phytane. The isoprenane contents in petroleum may vary as a function of the overall composition of the petroleum; the largest amounts of isoprenanes are present in paraffinic petroleums. In comparing quantitative contents of isoprenanes in different types of petroleum, account must also be taken of the deviations associated with the characteristics of the methods used to identify the hydrocarbons.

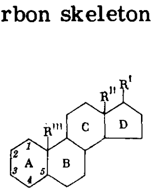
The majority of investigators assume, quite correctly, that the main source of isoprenanes is phytol, an unsaturated aliphatic alcohol, which can be isolated from plant chlorophyll by hydrolysis. Phytane (C_{20}) might have been formed from phytol under appropriate conditions by its dehydration and subsequent hydrogenation of the resulting unsaturated hydrocarbon. The thermocatalytic degradation of phytol itself or phytane (also with subsequent hydrogenation) might have led to the formation of hydrocarbons of this type[57,63,64]. This can be clearly illustrated by the following diagram[64]:



The experimental data for the thermocatalytic degradation of phytol and the composition of the petroleum isoprenanes confirm the validity of the above scheme. However, we may note that some of the isoprenanes might have been formed from the corresponding acids—fornesanoic, phytanic, etc., which have been detected in certain paraffinic types of petroleum.

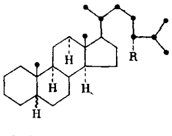
(c) Steranes and Triterpanes

Steranes are saturated tetracyclic hydrocarbons based, like steroids, on the carbon skeleton of cyclopentanoperhydrophenanthrene:



The origin of the steranes detected in petroleum and other caustobioliths is naturally associated with steroids. Steroids are substances of plant and animal origin, which differ in the nature of their substituents (they can contain hydroxy-, keto-, and other groups), the nature of the alkyl groups, and the degree of unsaturation of the tetracyclic nucleus. Thus steranes might have been formed from steroids as a result of a number of chemical transformations, among which reduction (under natural conditions, apparently associated with the disproportionation of hydrogen) should have played a significant role. The biological origin of steranes in fact made it possible to regard them, like isoprenanes, as biological "labels" and to relate the results of the study of petroleum steranes to the general problems of the origin of petroleum.

Steranes have been found in bituminous sedimentary rocks, in oil-bearing shales, in brown coal, and in petroleum. Here special attention must be made of the study of Nigerian petroleum and the oil-bearing shale from the Green River deposit (Colorado), the results of which have been described in reviews[65,66]. Cholestane, ergostane, and stigmastane have been detected in the 458–526°C fraction of Nigerian petroleum:

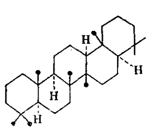


cholestane ($C_{27}H_{48}$), R = H;
ergostane ($C_{28}H_{50}$), R = CH_3;
stigmastane ($C_{29}H_{50}$), R = CH_2CH_3;

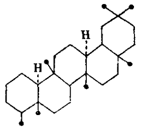
The same steranes, as well as lanostane, have been detected in the 450–500°C fractions of the Soviet petroleums from the Gyurgyansk [tentative transcription] and Anastasievsko-Troitsk [tentative transcription] deposits[67].

The hydrocarbon cholestane is an analogue of the steroid cholesterol {$C_{27}H_{46}O$, m.p. 149°C, $[\alpha]_D = -39°$}, which is one of the zoosterols, ergostane is an analogue of ergosterol {$C_{28}H_{50}$, m.p. 165°C, $[\alpha]_D = -130°$}, which is one of the microsterols, and stigmastane is an analogue of stigmasterol {$C_{29}H_{52}$, m.p. 170°C, $[\alpha]_D = -40°$}, which is a well known phytosterol.

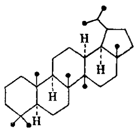
A number of analogues of cyclic polyterpenes, namely diterpanes (C_{20}) and triterpanes (C_{30}) have also been detected in petroleum (and other caustobioliths). The pentacyclic triterpanes detected included gammacerane, friedelane, and lupane:



gammacerane



friedelane



lupane

The presence in petroleum of hydrocarbons with the oleanane (a triterpane) structure has also been established.

Several triterpanes, which are solids melting at relatively high temperatures, have been isolated from Nigerian petroleum[68–70]. The triterpane gammacerane has been isolated from petroleum (and from the bitumen of the Green River shale) and has been thoroughly investigated by mass-spectrometry; it has a melting point of 290°C and $[\alpha]_{546}^{21} = +31.9 \pm 0.4°$.[69] Friedelane has been detected in the petroleums from the Gyurgyansk and Anastasievsko-Troitsk deposits[67]; the triterpanes lupane and moretane have been found in the Baku petroleum from the Surakhany deposit[71]. Furthermore, one should note that an unusual pentacyclic terpane, containing two rings with a spiro-junction, has also been found in Nigerian petroleum[70].

Since steroids and triterpanes consist of condensed alicyclic rings, there is a possibility of their stereoisomerism depending on the *cis*- and *trans*-disposition of the rings relative to one another, similar to the stereoisomerism of perhydrophenanthrene. In natural steroids, ring C occupies the *trans*-position relative to rings B and D, while ring A can have both *cis*- and the *trans*-configuration in relation to ring B. Indeed, it is proved possible to isolate from the Green River shale bitumen two isomers of cholestane, ergostane, and stigmastane in each case, namely the 5α- and 5β-isomers, depending on the position of the hydrogen atom at the fifth carbon atom. The 5β-isomer (*trans*-junction of rings A and B) usually predominates.

Like steroids, steranes are optically active, since the carbon atoms at the junctions between the rings are arranged asymmetrically. The latter should have led to a large number of stereoisomers. For example, pregnane (a C_{21} sterane) might have 128 isomers due to stereoisomerism alone, and, when two additional asymmetric centres are present (after the introduction of substituents into the ring), the number of possible isomers reaches 512. In reality, steroids are synthesised in nature with considerable selectivity and among the enormous number of steroids only four steric forms of the skeleton, corresponding to the energetically most favourable configuration, have been found. This naturally applies also to steranes.

The optical activity of steranes is of special interest. It has been noted for a long time that petroleums exhibit optical activity, which has served as a basis for the claim that petroleum contains components related to natural organic compounds with asymmetric molecules. The optical activity of petroleum is probably largely caused by the presence in the latter of sterane and triterpane hydrocarbons. More complete data on the optically active substances in petroleum can be found in Louis's paper[72].

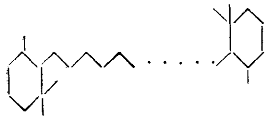
Different methods have been used to isolate and identify steranes and triterpanes. The concentrate of tetracyclic and pentacyclic hydrocarbons is isolated from the corresponding fraction containing branched paraffins and cycloparaffins using separation by thermal diffusion, adsorption chromatography on activated charcoal, gel-penetration chromatography on dextran, etc. Sterane (C_{27}, C_{28}, and C_{29}) and triterpane (C_{30}) concentrates are in their turn isolated from the resulting concentrate by preparative gas–liquid chromatography. Sterane concentrates are sometimes treated with thiourea in order to separate α(*trans*)- and β(*cis*)-steranes[73]. Steranes and triterpanes are identified by analytical gas–liquid chromatography, mass-spectrometry, and chromato-mass-spectrometry. The application of chromato-mass-spectrometry proved to be extremely effective, since the nature of the fragmentation of model steranes and triterpanes under the influence of electron impact had been thoroughly investigated beforehand[66].

It is noteworthy that the preparation of individual steranes and triterpanes, which are absolutely essential model hydrocarbons for their determination in petroleum, involves certain difficulties. The steranes described above (cholestane, ergostane, and stigmastane) are usually obtained from the corresponding sterols, containing double bonds and a hydroxy-group. Sterols are reduced under pressure in an atmosphere of hydrogen in the presence of catalysts or dehydration and hydrogenation are carried out in succession. It is then necessary to maintain reaction conditions such that the resulting saturated hydrocarbon (sterane) has a structure corresponding to that of the initial compound; in other words, one must make sure that there are no rearrangements and especially no rupture of the cyclopentane ring.

As already mentioned, steranes and terpanes have been found in various caustobioliths belonging to different, sometimes extremely ancient geological ages. The bituminous Green River shale, the steranes and triterpanes of which have been most thoroughly investigated, belongs to the Eocene Era in terms of its age (about 52 × 10^6 years). Steranes and terpanes have been detected in the organic material of more ancient sedimentary rocks in Precambrian deposits (more than 10^9 years old).

It is at present difficult to estimate quantitatively the content of steranes and terpanes in petroleum, since the majority of determinations have been qualitative. One can only note that the extract from the Green River bitumen, consisting of branched paraffins and cycloparaffins (average molecular weight 226–558) consisted to the extent of 10% of hydrocarbons of biological origin, among which there was 10% of isoprenanes, 20% of terpanes, and 20% of steranes. Steranes and triterpanes are probably also present in relatively large amounts in petroleum, at any rate in amounts comparable to that of isoprenanes.

Apart from isoprenanes, steranes, and triterpanes, other biogenic hydrocarbons have been detected in petroleum and other caustobioliths. These include, for example, perhydro-β-carotene[63,66]:



Perhydro-β-carotene ($C_{40}H_{56}$) is a hydrogenated analogue of β-carotene—a plant pigment.

In conclusion of this Section, one must note that further research on biogenic hydrocarbons from different types of petroleum will be useful not only for the extension of our knowledge of the chemical composition of petroleums, but also for the solution of geochemical problems of the origin of petroleum.

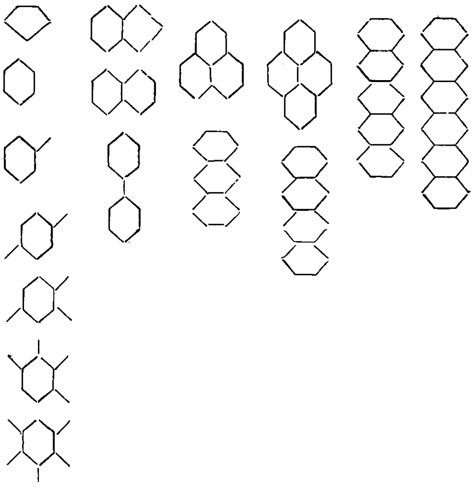
V. DETERMINATION OF THE OVERALL STRUCTURE OF INDIVIDUAL GROUPS OF HYDROCARBONS

The application of structural-group methods to the analysis of higher fractions of petroleum containing hydrocarbons with relatively high molecular weights was already noted above. These include, for example, the *n–d–M* method of van Nes and van Westen for the analysis of oil fractions of petroleum[74]. As a result of the extensive application of various methods for the separation of hydrocarbons and the use of spectroscopic research techniques, general and far-reaching characteristics of the structure of different groups of hydrocarbons can now be formulated over a wide range of boiling points.

Paraffinic hydrocarbons and naphthenes can be characterised, cyclopentane and cyclohexane rings can be determined, and the number of rings in the molecule, the number of substituents, and their size can be found from the mass and infrared spectra of the fractions isolated by the appropriate procedure. Mass-spectrometric, ultraviolet spectroscopic, and NMR methods are used to investigate aromatic hydrocarbons. It is then possible to establish the type of aromatic nucleus of the molecule (benzene, naphthalene, phenanthrene, etc.)[75]. The number of rings in polycyclic hydrocarbons and, in only a few instances, their positions have been determined by molecular spectroscopy.

A series of petroleums from different deposits, including fractions boiling at high temperatures (up to 470°C), have been investigated. The structural formulae (fragments) of the hydrocarbons which may be determined by modern methods are listed below. Polycycloparaffins and mixed hydrocarbons containing cyclohexane benzene rings are shown here by convention in the form of condensed systems.

Cyclanes



Aliphatic chains

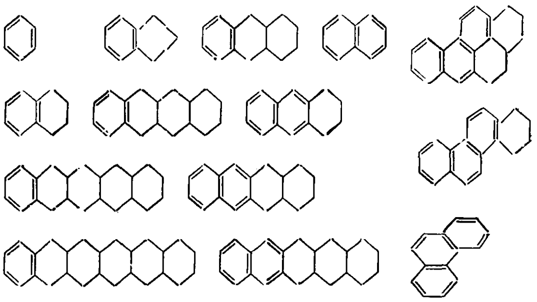
$—CH_2—$

$—CH_2—CH_2—$

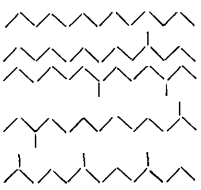
$—CH_2(CH_2)_nCH_2—$

$—CH_3$

Aromatic hydrocarbons



Alkanes



The general characteristics of petroleum hydrocarbons determined by the most modern research techniques are of considerable practical importance apart from their theoretical significance, since the results obtained can be used to assess the fractions processed into fuels and lubricating oils. At the same time, the general characteristics of the petroleum constitute a basis for subsequent more far-reaching research on specific types of hydrocarbons.

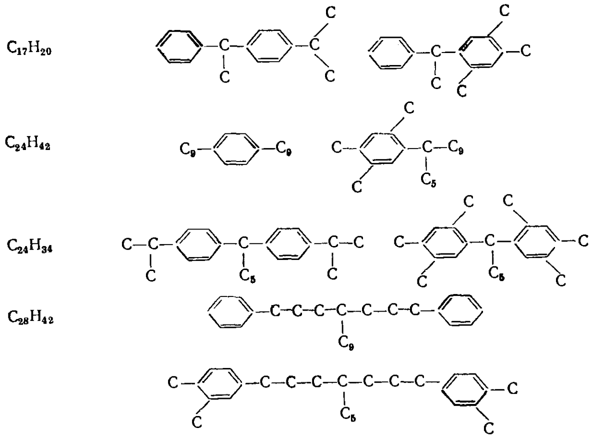
VI. CERTAIN REGULARITIES IN THE HYDROCARBON COMPOSITION OF PETROLEUM

The study of hydrocarbons from the middle and higher fractions of petroleum is extremely difficult owing to the presence in the latter of a large number of isomers. For this reason, chemists have endeavoured for a relatively long time to find regularities in the contents and distribution of various types of petroleum hydrocarbons; such regularities should be observed if the composition of petroleum is determined by certain general conditions governing its genesis from more or less similar organic material. The regularities would naturally facilitate also the investigation of the chemical composition of petroleum.

For example, one can reach an extremely important general conclusion about the composition of aromatic hydrocarbons in petroleum fractions. The studies by the American Petroleum Institute showed at one time that the hydrogenation of synthetic polycyclic hydrocarbons consisting of condensed benzene rings leads to the formation of cyclanes with a reduced viscosity and an enhanced viscosity index, while hydrogenation of aromatic hydrocarbons containing isolated benzene rings actually leads to an increase of viscosity and a decrease of the viscosity index[16,74,76]. It was established at the same time that the hydrogenation of narrow oil fractions leads to an appreciable reduction of their viscosity, which is greater the larger the number of benzene rings in the hydrocarbons. On this basis, it was concluded that polycyclic aromatic hydrocarbons in the oil fractions of petroleum virtually all belong to different kinds of condensed systems (see Rossini et al.[16], p. 327). For example, alkylated derivatives of anthracene, phenanthrene, and naphthacene are such "exceptional" types of polycyclic hydrocarbons, the hydrogenation of which results in a decrease of viscosity. However, it is known that naphthalene homologues containing long alkyl groups ($C_{18}-C_{26}$) behave on hydrogenation like the majority of aromatic hydrocarbons—their viscosity increases. Thus not all aromatic hydrocarbons with condensed benzene rings exhibit a decrease of viscosity on hydrogenation.

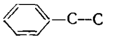
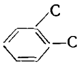
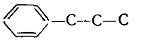
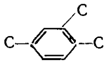
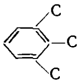
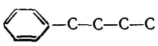
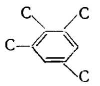
The study of the physicochemical properties of about fifty hydrocarbons, namely cyclohexane and benzene homologues, polycyclic (mainly bicyclic) C_{24} and C_{28} hydrocarbons (corresponding to the oil fractions of petroleum) provided grounds for a new interpretation of the structure of aromatic hydrocarbons in higher petroleum fractions[77,78]. It has been established that aromatic hydrocarbons containing methyl groups in the ring are in general anomalously viscous compared with other alkyl-substituted aromatic hydrocarbons having the same molecular weight. Aromatic hydrocarbons containing methyl groups have higher viscosities and refractive indices, smaller molecular volumes, and higher heats of evaporation. Table 5 lists the physicochemical characteristics of certain alkylbenzenes.

Similar relations have been obtained also for hydrocarbons with a different structure, differing in the number of methyl groups in the molecule; some of these are indicated below:



The increased viscosity of aromatic hydrocarbons with methyl groups in the benzene rings is due to increased intermolecular interaction (a relatively smaller molecular volume and a higher heat of evaporation). On hydrogenation, such hydrocarbons give rise to cyclanes, the viscosity of which is lower rather than higher than that of the initial aromatic hydrocarbons.

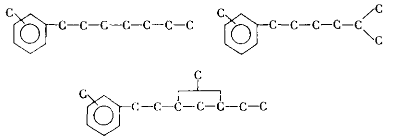
Table 5. Physicochemical characteristics of aromatic hydrocarbons.

Formula	Structure	ρ_4^{20}	n_D^{20}	Molecular volume, ml	Heat of evaporation, kcal mole^{-1}		Viscosity, cP	
					50° C	0° C	50° C	0° C
C_8H_{10}		0.8670	1.4959	122.5	9.70	10.35	0.48	0.87
C_8H_{10}		0.8802	1.5055	120.6	10.05	10.63	0.56	1.06
C_9H_{12}		0.8620	1.4920	139.5	10.65	11.18	0.58	1.18
C_9H_{12}		0.8758	1.5048	137.2	11.06	11.64	0.72	1.32
C_9H_{12}		0.8944	1.5139	134.6	11.31	11.86	0.82	1.82
$C_{10}H_{14}$		0.8601	1.4898	155.9	11.67	12.29	0.68	—
$C_{10}H_{14}$		0.8904	1.5130	150.7	12.77	13.35	0.82	1.86

Thus the decrease of viscosity on hydrogenation of petroleum fractions indicates primarily the presence in these fractions of considerable amounts of methyl-substituted aromatic hydrocarbons (including polycyclic condensed aromatic hydrocarbons). The cause of this characteristic of methyl-substituted aromatic hydrocarbons is unknown and requires separate examination. Here one can only note that the phenomenon of hyperconjugation has been observed for molecules containing methyl groups linked to the benzene ring, which may be reflected also in certain features of their physicochemical properties.

The conclusion reached concerning the structure of aromatic hydrocarbons in petroleum has been confirmed also by certain data obtained in direct studies on petroleum hydrocarbons. For example, C_{10} benzene homologues with methyl groups predominate among the aromatic hydrocarbons of Romashkino petroleum. On passing to higher petroleum fractions, the benzene homologues may contain also higher alkyl groups. According to non-Soviet investigators, hydrocarbons containing methyl groups and one larger alkyl group, do indeed predominate in the alkylbenzenes in petroleum[33].

Thus aromatic hydrocarbons, the alkylbenzenes in the light gas oil from American petroleum boiling in the range 230–305°C (from the Ponca deposit), have been investigated[33]. The light gas oil constituted 70% of the petroleum and the aromatic hydrocarbons isolated constituted 19.6% of the light gas oil. Adsorption chromatography on silica gel, adsorption on molecular sieves, and gas–liquid chromatography were used to isolate and separate the hydrocarbons; low-voltage mass-spectrometry and NMR were employed to determine the structure of the "average" molecule. It was established that the $C_{13}-C_{15}$ alkylbenzenes in the light gas oil consist mainly of di- and trisubstituted derivatives. The disubstituted alkylbenzenes usually contain one methyl group and one long C_7 or C_8 alkyl group in the 1,3- and 1,2-positions. The typical dialkylbenzenes can be represented as follows:



Two possible locations of the methyl group in the alkyl chain are indicated in the last formula.

A similar study of aromatic hydrocarbons containing a single benzene ring, isolated from the heavy gas oil and the light oil distillate (305–405°C) of the same petroleum, showed that these distillates contain approximately 75% of $C_{24}-C_{26}$ alkylbenzene with a single long alkyl group and several, sometimes three or four, methyl groups; some of these alkylbenzenes can also contain ethyl groups[34]. It is interesting to note that optically active $C_{25}-C_{26}$ hydrocarbons of the type of tetra- or penta-cyclanobenzenes with $[\alpha]_D^{25} = 6$ were detected in the same distillates.

Systematic research on petroleum hydrocarbons carried out in accordance with the programme of the American Petroleum Institute Project 6 permitted a number of conclusions concerning the hydrocarbon composition of different types of petroleum. Particular mention should be made of the conclusion that the relative quantitative contents of hydrocarbons within the limits of each type of hydrocarbons (straight-chain paraffins, branched paraffins, alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes) are approximately the same in different types of petroleum. Certain specific instances of this general conclusion have already been noted.

We shall now consider the possible cause of the above similarity of the compositions of different types of petroleum, namely whether this generalisation is applicable only to petrol fractions, whether it can be extended also to hydrocarbons with higher molecular weights, and whether it is valid for petroleums of sharply different ages.

It was noted a comparatively long time ago that petroleum consists of an equilibrium mixture of hydrocarbons formed as a result of various catalytic reactions occurring, for example, under the influence of aluminosilicates (natural clays) at certain temperatures near 150–250°C. Thus Frost[79] and Obryadchikov[80] established for the first time that the contents of cyclohexane and methylcyclopentane in a wide variety of petroleums corresponded to their equilibrium concentrations at temperatures in the range ~150° to 300°C.

The relative equilibrium concentrations of cyclohexane and methylcyclopentane (the K_e values) at different temperatures between 150° and 300°C are as follows:

T, °C	K_e
150	1.38
200	0.89
250	0.63
300	0.48

Approximately the same relations are observed also for the contents of both hydrocarbons in different types of petroleum. The knowledge of the temperatures in the formation of petroleum with allowance for the possible transformations of hydrocarbons (or the initial compounds) under the influence of natural catalysts of the aluminosilicate type seemingly might have accounted for the differences between the chemical compositions of different types of petroleum and might have led to the discovery of new possibilities for the investigation of the chemical composition of petroleum itself. Having established the equilibrium proportions of the hydrocarbons within the limits of the particular group at a given temperature, for example at 200°C, and having determined the thermodynamically most stable structures of the hydrocarbons, it might be possible to predict beforehand their contents and proportions in petroleum; this would be particularly useful in the determination of the contents in petroleum of the structural and steric isomers of different types of hydrocarbons.

There are a number of publications on the stereochemistry and relative stabilities of hydrocarbons[46,64,81,82]. The stereochemistry and equilibrium proportions (relative stabilities) of a series of C_7-C_9 alkylcyclopentanes, C_8-C_{12} alkylcyclohexanes, various C_8-C_{10} bicyclanes, $C_{11}-C_{12}$ alkyldecalins, and $C_{11}-C_{13}$ alkyladamantanes have now been investigated. The conformational characteristics of alkanes and cyclanes are being widely studied.

The results obtained are undoubtedly valuable for the characterisation of certain types of hydrocarbons and for their determination in petroleum. For example, in many instances it has indeed been found that the thermodynamically most stable bicyclanes predominate in petroleum.

The study of the relative stabilities of the isomeric forms of methylbicyclo[3,2,1]octanes and methylbicyclo-[2,2,1]octanes in synthetic model hydrocarbons[83] permitted the subsequent identification of nine methylbicyclo[3,2,1]-octanes and methylbicyclo[2,2,2]octanes in Soviet petroleums of different origins. It was established that, among identified hydrocarbons of the 125–150°C fraction of the Gryazevaya Sopka petroleum[84] and the 70–180°C fraction of Balakhansk petroleum[85], the most stable 1-methylbicyclo[3,2,1]octane is present in the largest amount, while the contents in the petroleums of the relatively less stable 2,3- and 6-substituted methylbicyclo[3,2,1]octanes are smaller. There are other examples of this kind.

Thus the above type of research on hydrocarbons, based on the determination of the equilibrium proportions of hydrocarbons and their relative thermodynamic stabilities at specific temperatures, yields valuable evidence for subsequent direct studies on petroleum hydrocarbons.

At the same time one must note that the limits of the applicability of this approach to the investigation of petroleum hydrocarbons are still not clear. It is not known which types of hydrocarbons are present in petroleum in equilibrium proportions corresponding to a specific temperature. Nor can the temperature limits corresponding to the formation of petroleum hydrocarbons be regarded as rigorously established. The thermodynamic stability of hydrocarbons depends to a large extent on temperature.

Presumably petroleum contains three groups of hydrocarbons. The first includes biogenic hydrocarbons which retain the structure of the initial natural products, for example, isoprenanes, steranes, triterpanes, and other still unknown hydrocarbons, the proportions of which may not, of course, correspond to equilibrium. They are determined by the contents of the natural products in the initial material from which petroleum originated. The hydrocarbons whose proportions correspond to equilibrium (at a specific temperature) may be included in the second group; the third group consists of hydrocarbons formed as a result of a number of transformations which do not retain the initial structure and whose composition does not correspond to equilibrium for one reason or another, which has not as yet been elucidated. One must bear in mind that the proportions of hydrocarbons might have altered also as a result of secondary processes (adsorption on rocks, particularly during the migration of petroleum, etc.).

Further research on biogenic petroleum hydrocarbons and the determination of the types of hydrocarbons whose proportions may correspond to equilibrium is necessary; this requires in its turn further far-reaching investigation of the hydrocarbon composition of petroleum as a whole. Such research will make it possible also to obtain more refined data on one of the most important problems in the geochemistry of petroleum—the problem of the temperatures at which petroleum was formed.

The discussion of these aspects of the hydrocarbon composition of petroleum frequently involved certain problems which have some bearing on the origin of petroleum. It is becoming increasingly necessary that investigators concerned with the study of the chemical composition of petroleum should examine new data on its composition from the standpoint of general modern ideas about its origin. The most important generalisations will probably be made on these lines.

The present review has dealt only with certain problems associated with the investigation of petroleum hydrocarbons and petroleum fractions. The extremely important questions in the field of petroleum chemistry, such as the investigation of the chemical composition of the oil fractions and lubricating oils, the study of high-molecular-weight compounds (including hydrocarbons) in petroleum, and others require separate consideration.

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Heteroatomic Components of Petroleum

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The state of the problem of the isolation, separation, and characterisation of the heteroatomic compounds of petroleum is examined and current data on the chromatographic and mass-spectrometric characteristics of organosulphur compounds in petroleum and petroleum products are surveyed. The results obtained in studies on the composition and structures of sulphides and thiophens in distillates and residual petroleum fractions are listed and the fundamental data on the oxidation of middle petroleum fraction sulphides to sulphoxides and sulphones and on the pathways followed in their further chemical transformation are compiled. Certain aspects of the utilisation of petroleum sulphides and sulphoxides in the national economy are considered. The bibliography includes 210 references.

CONTENTS

I. INTRODUCTION

Modern experimental techniques have made it possible to compile information about the characteristics of the composition of complex natural formations such as petroleum and bitumens. The hydrocarbons contained in such substances have been investigated in detail. Fine instrumental analytical methods for the investigation of the compositions, structures, and properties of organic compounds and their multicomponent mixtures have been developing vigorously during the last 5–10 years. Intensive investigation of the heteroatomic components of petroleum and bitumens has been particularly characteristic of this period.

The interest in heteroatomic compounds (HAC) of petroleum is due to a number of causes: the fraction of petroleums rich in HAC has increased sharply in the world production and processing of petroleum; in the manufacture of fuel and lubricating oil, the majority of HAC constitute a harmful admixture hindering the processing of the raw material and lowering the quality of the commercial products; the HAC are responsible for the formation and stabilisation of water–petroleum emulsions on the way from the borehole to the refinery; the study of the HAC helps to approach more closely the solution of the problems of the origin of petroleum and its transformations underground and the solution of the associated problem of the distribution of petroleums of particular quality in the deposits. In other words, the knowledge of the HAC constitutes a basis for the geochemical prediction of the available raw material resources for the petrochemical processing of petroleum. Such processing has been tending to replace the production of fuel and lubricating oil at an increasing rate. The value of the petroleum HAC is also of considerable interest for fundamental science. The chemical composition and structure of the majority of the petroleum HAC were unknown. The determination of the relation between the HAC and the petroleum hydrocarbons, on the one hand, and the parent material of petroleum, on the other, is one of the most interesting problems of modern biogeochemistry.

An attempt will be made below to describe briefly certain results of studies in the past five years and, in relation to specific problems, the last ten years (from 1966 to 1976). One should note that this period has been characterised by a still unduly analytical approach to the solution of the problem of the composition of petroleum. The following factors require constant attention: the complex combination of the acid–base and oxidation–reduction properties of petroleum hydrocarbons; the characteristic donor–acceptor interactions of the HAC with condensed aromatic hydrocarbons; the problem of the colloidal, supermolecular structure of petroleum and the role of the HAC in its changes; the involvement of charge-transfer complex and clathrate compound formation in the organisation of short-range order leading to structure formation in petroleums, which has not been considered hitherto in any way at all.

II. METHODS FOR THE ISOLATION OF HETEROATOMIC COMPOUNDS FROM PETROLEUM AND PETROLEUM PRODUCTS

Crude petroleum is characterised primarily by its elemental composition and the limits of its boiling point range corresponding to the distribution of the components with respect to their molecular weights. The elemental compositions of all petroleums are distinguished by the predominance of carbon and hydrogen, which are the main constituents not only of hydrocarbons but also of all heteroatomic compounds in petroleum. The latter are in most instances monofunctional; a more detailed study led to the discovery of the presence in petroleums of a large number of bi- and tri-functional compounds but at negligibly low concentrations. The content of carbon in petroleum is in most cases restricted to the range 80 to 87%, of hydrogen to 11–14%, of sulphur to 0.01–0.1% (up to 8% in sulphur-containing and high sulphur petroleums), and of nitrogen to 0.04–0.6% (unique petroleums with an increased nitrogen content are known). The data on the oxygen content are in most instances insufficiently accurate, since they have frequently not been obtained by direct analysis but by difference (the errors in the determination of all the remaining elements naturally accumulate under these conditions in the calculated oxygen content); nevertheless, one can assume that the oxygen content varies in the range 0.2–7.0%, i.e. is of the same order of magnitude as the sulphur content and an order of magnitude higher than the nitrogen content. The overall content of all the remaining elements in petroleums is usually less than 1%. Most of the residue consists of vanadium derivatives.

The simplest and oldest method for the resolution of petroleums into fractions is based on their boiling points. To a first approximation, this corresponds to the distribution of the components with respect to their molecular weights in view of the validity of the expression $T \simeq aM^b$, where T is the boiling point (on the Kelvin scale) and a and b are constants[1,2]. In most cases b differs little from 2, i.e. $T \simeq a\sqrt{M}$; a varies within wide limits (from 36 to 48 for hydrocarbons), being correlated with the particular homologous series to which the compound belongs (with the value of x in the formula $C_nH_{2n} \pm x$ proposed by Mendeleev[3]) and with the characteristics of the heteroatoms present. When petroleum or petroleum products are distilled with the aid of relatively inefficient fractionating devices (still widely used to determine the standard characteristics of commercial products), the distribution of the components with respect to their melting points in the multicomponent fractions collected is nearly Gaussian[4].

An increase in the efficiency of fractionation entails a marked decrease of the number of compounds included in the fractions collected and in the limit leads to the isolation of individual compounds; this rules out a statistical approach to the characterisation of narrow fractions. The latter is shown particularly clearly in attempts to extend to narrow fractions the statistical methods for the analysis of composition, particularly those proposed by Waterman et al.[5] for commercial petroleum products and broad petroleum fractions. Nevertheless there is no doubt that fractionation to give comparatively broad fractions is at present useful for a preliminary resolution of petroleum and petroleum products. It is useful to set limits to the fractions collected on the basis of the structural transitions of the components, for example from alkanes to monocyclic compounds, from monocyclic to bicyclic compounds, and from the latter to polycyclic compounds.

The employment of highly efficient chromatographic devices and of mass spectrometry in the next separation stage permits the recommendation that one abandons the preliminary separation of test materials by fractionation into extremely narrow fractions, which is still used. The collossal multiplicity of the components of the middle and high petroleum fractions requires the application of the methods of group and structural-group analysis, including functional analysis, and not individual analytical techniques. In many spectroscopic, refractometric, and other physical methods for structural-group analysis, one uses the atomic or bond increments (frequencies, intensities, refractions, dispersions, etc.) obtained by averaging the data for a multiplicity of individual compounds of different structures. Naturally, the application of these increments to compounds with restricted compositions without due allowance for their characteristics may lead to an increase of error in the determination of the composition. We shall return to this problem below when modern chromatographic mass-spectrometric methods for the analysis of petroleum distillates are considered.

The distribution of the petroleum components with respect to molecular weight is different for different types of petroleum. Petroleums from gas-condensate deposits and petroleums which have undergone the greatest geochemical transformations under reducing conditions are enriched in the light components. Petroleums which have undergone least geometrical modification under reducing conditions or which have undergone oxidation transformations are enriched in the heavy components. The same group includes petroleums greatly enriched in tars and asphaltenes, which have undergone the stage of retrograde condensation accompanied by the elimination of the light fraction, which under suitable conditions might have formed gas-condensate deposits.

In conformity with all the foregoing factors, the distribution of petroleum heteroatomic compounds among its fractions varies just as strongly. Heavy petroleums are usually richest in the HAC. For a more correct understanding of this phenomenon, it is necessary to consider the differentiation of petroleums not only with respect to their boiling points but also with respect to their "component composition", which was introduced into practical technical analysis of petroleums as early as the beginning of this century by Richardson[6] and, independently, by Marcusson[7].

After the distillation of light-coloured petroleum products and dilution of the residue with benzene, asphaltogenic acids and then their anhydrides are extracted (by Marcusson's method) from the heavy component of petroleum. This is followed by the deposition of asphaltenes, carbenes, and carboids, heavy oils are eliminated from the residue, and petroleum tars ("silica gel" tars according to the method of their isolation) are obtained. This method of separation has been described in detail by Nametkin[8], who also indicates simplified versions of the method recommended by Sakhanov[9] and refined by Starostin and Boldyreva[10]. The essential feature of the simplification consists in the abandonment of the isolation of asphaltogenic acids and their anhydrides from asphaltenes. This version of the method has been widely adopted. Subsequently it was supplemented by the desorption of oils and tars from the silica gel by a series of solvents of increasing polarity, which made it possible to differentiate the oil fraction into saturated and aromatic fractions with increasing contents of heteroatomatic compounds. The development of component analysis is described in greater detail by Sergienko[11].

All the versions of the methods of component analysis considered involve the precipitation of asphaltenes by solvents of low polarity and the sorption of tars on silica gels, alumina, natural bentonite clays, or zeolites (for a description of the latter, see Benashvili[12]). It is then assumed that the majority of the heteroatoms detected in the tars and asphaltenes isolated are present as structural elements in molecules of high-molecular-weight compounds, being linked to them by σ bonds. However, sufficiently convincing evidence for this view has not so far been adduced. Our own observations make it necessary to assume that, together with the heteroatoms entering into the composition of asphaltenes and tars with formation of classical bonds, heteroatoms in comparatively low-molecular-weight compounds, sorbed both on silica gel and on macromolecular formations generated by tars and asphaltenes, play a significant role. The stability of the supermolecular formations formed is determined under these conditions not only by the donor–acceptor interactions with participation of the heteroatom but also by the similarity of the structures of the hydrocarbon fragments of the moieties enriched in condensed aromatic and naphthenoaromatic rings. Nor can one exclude the role of the formation of clathrate compounds by low-molecular-weight components with macromolecular components, the former being enclosed in hollow structural cells of the latter.

The characteristics of the elemental, component, and fractional compositions of the petroleums in the Soviet Union are described in a handbook[13], the majority of the data in which have been obtained by unified methods and are comparable. The same handbook quotes the structural-group characteristics of the light-coloured distillates and the compositions of the majority of petrols in terms of individual hydrocarbons.

The functional characteristics and the content of sulphur and its derivatives in petroleums from the Urals-Volga region and Siberia have been determined by Obolentsev and Baikova[14], also using unified methods. Their monograph[14] includes data concerning the presence of free, hydrogen sulphide, mercaptan, disulphide, and sulphide sulphur in fractions which begin to boil at temperatures up to 120°C, in the ranges 120–200°C, 200–250°C, and 250–300°C, and in narrow (approximately 3 K fractions) of a number of petroleums in the USSR as well as data concerning the presence of free, mercaptan, and sulphide sulphur in the initial petroleums. The monograph also contains information about the overall sulphur content, which makes it possible to deduce the presence of "residual sulphur", contained mainly in compounds belonging to the thiophen and diaryl sulphide series. Unfortunately, the authors[14] do not characterise the residues boiling above 300°C (even their yield is not quoted). The monograph lists the characteristics of a number of petroleums and fractions relating to the threshold of thermal stability, indicating the presence of thermally unstable compounds (determined using the method adopted by Coleman et al.[15]), and the analytical methods used are described.

The distribution of sulphur and nitrogen among the component fractions of the petroleums from the Urals-Volga region and Western Siberia was recently reported by Eigenson and Ivchenko[16], who established that, after the distillation of fractions boiling up to 450°C (containing about 60% of all the sulphur present in petroleum), the sulphur in the residue is present to the extent of 36–40% in oils, 42–46% in tars, and 15–20% in asphaltenes. The distribution of nitrogen is markedly different: the residue contains about 90% of the amount present in the initial raw material; the oils in the residue contain only 4–8% of the nitrogen, the tars 52–63%, and asphaltenes 37–42%. This is apparently associated with the relatively higher reactivity of the nitrogen compounds, leading to their association in the form of salts and complexes with the oxygen-containing components of petroleum—primarily acids and phenols. The overall nitrogen content is approximately an order of magnitude lower than the content of sulphur in these petroleums.

An interesting version of the component semimicro-analysis of petroleum was achieved by Pozdyshev et al.[17]: light hydrocarbons were extracted with a 1 : 4 methanol-acetone mixture; a 10% NaCl solution precipitates from the extract light oils with an admixture of surface-active comparatively low-molecular-weight heteroatomic compounds, which can be extracted with water. The residual tar ("Goudron") remaining after the extraction of the light oils was deposited on paper, from which heavy oils were extracted with isopropyl alcohol; after this, tars were extracted with boiling hexane and asphaltenes with boiling benzene. The method yielded data in satisfactory agreement with the results obtained in the usual way.

The petroleums from the deposits in the Western Siberian, Urals-Volga, and Western Kazakhstan regions (the Ust-Balyk, Pravdinsk, Megionsk, Uzen'sk, Romashkino, Arlansk [tentative transcription], Pokrovsk, and Mukhanovsk deposits) were investigated by this micromethod. The limits of variation of the compositions of these petroleums were found: 26–77% of light oils (with the average molecular weight M = 190–241); 10–49% of heavy oils (M = 311–603); 2–14% of tars (M = 577–1059); 0.2–4.4% of asphaltenes (M = 886–3298). The light transmission constants [presumably ϵ_λ values (Ed. of Translation)] of the crude petroleums and oils are similar and vary in the range 162–660; the corresponding ranges for tars and asphaltenes are 1964–3670 and 4106–15 000 respectively. The method proposed will presumably prove useful for the investigation of heteroatomic compounds in petroleum in combination with modern gas-chromatographic elemental microanalysis.

Purely chemical methods for the separation of petroleum components, based on the reactions of functional groups, are the most important for the isolation, separation, and identification of the heteroatomic components of petroleum and petroleum products. Here we shall recall the extraction from petroleum of nitrogen-containing bases by acids, the subsequent extraction of carboxylic acids with sodium carbonate, the extraction of phenols with strong alkalis, and the re-extraction of the bases liberated on hydrolysis of the salts which they have formed with petroleum acids. Since the present author and Musaev applied this method for the first time[18] in order to characterise the relation between the properties of light petroleum hydrocarbons (from deposits of different ages) and those of non-hydrocarbon components—bases, acids, tars, and asphaltenes†—it has not altered fundamentally.

It has been suggested that *o*-sulphobenzoic and sulphosalicylic acids[20] in the form of 10% aqueous solutions and in the anhydrous state be used instead of inorganic acids for the extraction of bases from fuel fractions. The extraction of bases is accompanied under these conditions by the transfer of some of the acids to the hydrocarbon phase and the elimination of acids from the extract is difficult. An important advance was the use of ion-exchange resins (anion and cation exchangers) for the selective extraction of compounds with acid and basic functions. As long as the aim of the investigations was to free the petroleum products from these components, the main task involved quantitative sorption and did not present special difficulties. Following the development of research devoted specifically to the heteroatomic components of petroleum, attention had to be concentrated on the much more difficult problem of the quantitative desorption of the test compounds in an unchanged form.

The coarsely porous sulphonic acid cation-exchange resins KU-2 and KU-23 (styrene-divinylbenzene copolymers) have been used[22–25] for the extraction of nitrogen-containing bases from crude petroleums and distillates. According to Bezinger et al.[23], the following method has been recommended for the preparation of

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†This study was carried out in connection with the investigation of the role of surfactants in crude petroleums in the displacement of petroleum by water and in the formation of emulsions, carried out by Zinchenko in consultation with Rebinder and Kusakov. Evidently the suggestion[19] that the first studies on surfactants in crude petroleum were made in 1946[20] is erroneous.

nitrogen-containing concentrates from petroleum: a benzene solution of petroleum is treated with a cation exchanger and filtered, acetic anhydride and a portion of fresh cation exchanger being added to the filtrate in order to increase the sorbability of the nitrogen-containing bases on the cation-exchange resins. The rate and degree of extraction of the bases increase greatly under these conditions (one must bear in mind that the capacity of the cation exchanger with acetic anhydride is appreciably reduced). The role of acetic anhydride is in this case probably the same as in non-aqueous titration in differentiating solvents. However, one cannot rule out the possibility that acetic anhydride binds a proportion of the heteroatomic petroleum components, blocking the nitrogen of certain bases. Such ideas are supported by the finding that a similar effect can be obtained on replacing acetic anhydride by dimethylformamide.

The stepwise separation of chemisorbed bases into those extractable by benzene and ethanol, recommended by Bezinger et al.[23], is not obligatory. A series of solvents of increasing polarity can be used for selective desorption, particularly when one can postulate the presence in the mixture of compounds differing in their basicity. The complete extraction of all the bases by a highly polar solvent is also feasible. In experiments with distillates containing an appreciable amount of sulphides, it is best to convert them first into sulphoxides in order to facilitate their separation from nitrogen-containing bases on the cation-exchange resin.

The proposed version of the isolation of bases with the aid of acetic anhydride is naturally applicable only to petroleum and products which do not contain appreciable amounts of primary and secondary bases capable of chemical interaction with this reagent (acylation).

A procedure resembling the isolation of petroleum bases is the extraction of organic sulphides from petroleum distillates with sulphuric acid. There are no fundamental differences: both nitrogen and sulphur compounds of the above groups are freely converted into 'onium forms, which are readily hydrolysed with regeneration of the initial amines and sulphides:

$$R_3N + HA \rightleftarrows R_3NH^{\oplus}A^{\ominus} \quad ,$$

$$R_2S + HA \underset{H_2O}{\rightleftarrows} R_2SH^{\oplus}A^{\ominus} \quad .$$

The growth of interest during the last decade in the isolation of large amounts of sulphides from middle petroleum fractions stimulated vigorous research on their extraction with sulphuric acid. A version of the sulphuric acid method for the preparation of sulphide-aromatic concentrates has been proposed by Chertkov, Spirkin, and Demishev[26,27]. Subsequently, this procedure was frequently tested and refined[28,29], and has reached a stage where it can be applied on an experimental-industrial scale. The method is widely used in studies in the USSR on the sulphides of middle petroleum fractions[30].

The much lower basicity of sulphides (compared with nitrogen-containing components) and their higher concentration preclude their isolation in a pure form: sulphide-aromatic concentrates are always obtained. The same happens in sorption methods for the isolation and separation of heteroatomic petroleum compounds on silica gels, alumina, and other acid or amphoteric oxides. Certain differences between the concentrates obtained (a reduced content of light dialkylsulphides and an increased degree of extraction of thiophens into the sulphuric acid concentrate) have been examined[31].

The formation of hydrogen bonds of different types probably plays an important role in the formation of sulphide-aromatic concentrates[32]. The tendency of sulphides to form associated species with condensed aromatic compounds, recently investigated in model systems[33-35], is undoubtedly also significant[32]. It has been shown that such species are formed only by aromatic sulphides and aromatic hydrocarbons and it has been suggested that the type of association is the same as that observed in purely hydrocarbon systems. Associated species, mainly with 1:2 composition, have been observed for the latter in binary systems, while the component ratio in the associated species in sulphide-hydrocarbon systems is 1:1.

The characteristic features of the solubility of organosulphur compounds and the possibility of their isolation and separation by extraction are directly related to the characteristic features of the complex formation process. On the basis of studies of the solubilities of 30 sulphides in 24 organic solvents, Obolentsev et al.[36] divided solvents into three groups: in the first group, the solvent power depends little on the molecular weight of the sulphur compound (acetylacetone, propyl alcohol); in the second group, the solvent power varies sharply with the molecular weight; the solvents of the third group tend to dissolve selectively specific types of sulphur compounds. The study was performed by determining the consolute temperatures. In the experimental temperature ranges, the composition–temperature curves pass through a distinct maximum, with the exception of the systems formed by alkylthiophans and 2-butylthiophen with ethanol. These anomalous systems were not investigated in greater detail.

Following the development of gas-chromatographic methods for the determination of the physicochemical characteristics of organic liquids, their volatilities, activities, and extraction characteristics[37], simple and rapid methods for the estimation of the selectivities of extractants for heteroatomic compounds became possible. The relative selectivities of tens of extractants[38] have been calculated for the simplest model systems (thiophan, di-isopropyl sulphide, and hexanethiol) using literature data[39,40]. The activity coefficients (in the temperature range 60–80°C) of four alkanethiols (C_4–C_8 and six dialkyl sulphides (C_3–C_{10}), thiophan, thiophen, and 2- and 3-methylthiophens have been published[38] and the relative selectivities[41] in the separation of light sulphur compounds and hydrocarbons have been calculated. It has been shown in a report[39] covering data for 28 solvents that phenol is the best extractant for the separation of aliphatic and cyclic sulphides.

The donor–acceptor interaction of heteroaromatic compounds with metal cations and their capacity for complex formation have been known for a long time. Mercaptans and sulphides are frequently isolated from light-coloured petroleum distillates and characterised with the aid of mercury(II) salts [mercury(II) chloride and acetate]. In particular, this method has been used in Nametkin's laboratory. Nametkin always showed much interest in heteroatomic petroleum compounds, particularly in sulphur compounds. The first dissertation devoted to the sulphur compounds in petroleum from the Ishimbai deposit[42] as well as a number of reports dealing with studies on sulphur compounds in other petroleums[43-45] originated in his laboratory. Sulphur compounds were isolated and purified in these investigations via their mercury complexes. Such complexes are still being used for analytical purposes.

Systematic studies on the formation of complexes by organosulphur compounds with a number of metals were begun in 1960 in Obolentsev's laboratory. The first series of studies devoted to complexes with mercury salts was carried out by Lyapina[46]. She established that a donor–acceptor bond is formed by sulphur in complexes of dialkyl sulphides and thiacyclanes with mercury(II) bromide and found that the energies of the bonds formed by the same sulphides with mercury(II) acetate are in the narrow range 10.5–1..5 kcal mole^{-1}. It has been shown that the equilibrium yield of the complexes falls with increase of the molecular weight of the sulphides and with decrease of their symmetry. The composition of stable mercury(II) acetate complexes were found to be 1 : 2 for ten sulphides and 1 : 1 for twenty sulphides. The small differences between the heats of formation of the 1 : 1 and 1 : 2 complexes led to the hypothesis that the nature of the bond formed by the second mercury(II) acetate molecule with the sulphide differs from the donor–acceptor linkage between the sulphide and a single mercury(II) acetate molecule. The majority of saturated sulphides form stable 1 : 2 complexes with mercury(II) bromide. The electron-donating capacity of aryl and diaryl sulphides is sharply reduced.

The complexes of mercury(II) halides with dialkyl sulphides are best precipitated from alcoholic solutions and those of thiacyclanes from ethereal solutions. The methods of dielectric-constant and cryoscopic titrations, developed by Gur'yanova[47], were widely used in the above investigation in relation to a wide variety of complexes of organic compounds. The formation of complexes of sulphides having different structures with tin tetrachloride[48] and with iodine[49] had been investigated previously. A decrease of the tendency by the organic sulphides towards complex formation on passing from saturated to aromatic compounds was noted.

Using the method of cryoscopic titration, Gur'yanova et al.[50] investigated the formation of complexes by the sulphides in sulphuric acid concentrates with aluminium, gallium, tin, and titanium halides and with iodine. They found that all the sulphides extracted with 86% acid from the 150–325°C fraction of Arlansk petroleum form 1 : 1 complexes with $AlCl_3$ and $GaCl_3$; about 90% of these sulphides form 1 : 2 complexes with $SnCl_4$ and $TiCl_4$, while about 10% do not react. The heats of formation of the $SnCl_4$ complexes with dialkyl sulphides are about 12.6 kcal mole^{-1}, while those for the formation of complexes with the sulphides in the concentrate investigated are only 7.6 kcal mole^{-1}. This is probably associated with the presence in the latter of aromatic sterically hindered dialkyl sulphides and α-substituted thiacyclanes. More than 90% of the sulphides isolated from the same distillate by treatment with 91% sulphuric acid formed 1 : 1 complexes with $AlBr_3$, $GaCl_3$, and iodine and 1 : 2 complexes with $SnCl_4$. Near ultraviolet spectroscopy demonstrated the presence of aromatic compounds in these sulphides; they probably include alkyl aryl sulphides and admixtures of thiophens.

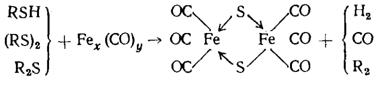
The formation of complexes by sulphides with silver nitrate[51] was investigated by Ben'kovskii and coworkers[52–55] in order to obtain pure sulphides from sulphide concentrates and for their differentiation. Complexes of 28 individual sulphides with $AgNO_3$ were investigated. Dialkyl sulphides (thia-alkanes) form 1 : 1 complexes, while thiacyclanes form both 1 : 1 and 1 : 2 complexes (mono- and di-solvates). The latter is probably due to the rigidity of the carbon–carbon bonds in thiacyclanes. The melting points of the thiacyclane complexes are much higher than those of the complexes of thia-alkanes having a similar composition. A method permitting quantitative separation of sulphides from thiophens and hydrocarbon admixtures present in sulphuric acid concentrates has been developed on model mixtures. The sulphides were regenerated from the complexes with 20% aqueous ammonia. Approximately 73% of the saturated sulphides and 24% of a mixture of thiophens and hydrocarbons were isolated from the concentrate of the 150–250°C fraction of Arlansk petroleum with the aid of silver nitrate.

The study of the solubilities of the individual complexes of sulphides with silver nitrate showed that derivatives of thia-alkanes and α-substituted thiacyclanes dissolve in aromatic hydrocarbons and alcochols much more effectively than β-substituted thiacyclanes. The possibility, in principle, of the quantitative separation of sulphides having similar properties by formation of complexes with $AgNO_3$ and subsequent extraction of the mixture of complexes with toluene has been demonstrated for binary mixtures (6-thiaundecane–3-pentylthiophan and 2-pentylthiophan–3-pentylthiophan).[53]

Saturated sulphides have been separated from aromatic sulphides present in the higher fractions of the Dzhar-Kurgan high-sulphur petroleum by the formation of complexes with silver nitrate. This made it possible to concentrate aryl sulphides and to detect for the first time the presence in the petroleum of alkyl benzyl and alkyl naphthyl sulphides[56]. The experience gained in our laboratory also demonstrated the suitability of the method employing $AgNO_3$ for the preparation of pure saturated sulphides.

The evident unsuitability of silver nitrate as a reagent for the isolation of sulphides and their elimination from petroleum products on a large preparative scale is evident.

In the search for more readily available complex-forming agents, Nametkin and coworkers made systematic studies on reactions with iron carbonyls. They considered reactions via the mechanism[57]



where $x = 1$ and $y = 5$, $x = 2$ and $y = 5$, or $x = 3$ and $y = 12$.

Table 1. The interaction of mercaptans, disulphides, and sulphides with iron carbonyls*.

Iron carbonyl	Yield of complexes, wt.% (time, h)		
	RSH	$(R'S)_2$	R''_2S
$Fe_3(CO)_{12}$	95—98 (1)	72—76 (5)	60—64 (18)
$Fe_2(CO)_9$	90—93 (11)	65—67 (19)	50—54 (24)
$Fe(CO)_5$	59—61 (22)	54—59 (34)	20—25 (36)

*R = Ethyl, n-butyl, n-hexyl, n-dodecyl, phenyl, or benzene; R′ = n-butyl, n-pentyl, n-hexyl, or n-dodecyl; R″ = methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-dodecyl, cyclopentyl, or phenyl.

Data for the degrees of reaction of individual compounds were obtained and are listed in Table 1, which shows that the limits of variation of the yield of each carbonyl within groups of sulphur compounds are relatively insensitive to the structure of their hydrocarbon base. This made it possible to employ a single procedure for the estimation of relative reactivities, based on the method of the competing reactions of iron dodecacarbonyl with hexyl derivatives of sulphur, in accordance with the following scheme:

$$\left.\begin{matrix} 6\,C_6H_{13}SH \\ 3\,(C_6H_{13}S)_2 \\ 6\,(C_6H_{13})_2S \end{matrix}\right\} 2\,Fe_3(CO)_{12} \rightarrow [Fe(CO)_3SR]_2 + \left\{\begin{matrix} 3\,H_2 \\ 6\,CO \\ 3R_2 \end{matrix}\right. .$$

Having assumed that the value for the sulphide is unity, the authors[57] found that the relative reactivity decreases in the sequence $RSH > RS_2R > R_2S$ (in proportions of 13 : 9 : 1), in agreement with the data in Table 1, from which follows the following series of the reactivities of the carbonyls in the above reactions:

$$Fe_3(CO)_{12} > Fe(CO)_9 > Fe(CO)_5 .$$

In conformity with previous studies[58,59], Nametkin et al.[57] believe that the above reactivity series for iron carbonyls is correlated with the ease of formation on thermal decomposition of the coordination-unsaturated intermediate compound $[Fe(CO)_4]^*$.

In the next communication[60], it was shown that the petrol and kerosine-gas oil petroleum distillates and the products of the thermal and thermal-catalytic processing of petroleum can be completely freed from hydrogen sulphide, mercaptans, disulphides, and free sulphur and, to the extent of 20–50%, from other organic sulphur, nitrogen and oxygen compounds with the aid of iron carbonyls, dipentadienylnickel, di(ethylphenyl)chromium, and other complexes of transition metals in their lowest valence forms. Table 2 presents data illustrating the elimination of organosulphur compounds from various petroleum products.

Table 2. The desulphurisaton of petroleum products by low-valence transition metal complexes.

Petroleum products	Fraction, °C	Complexes	$[S]\cdot 10^3$, % total content initial	total content in purified fraction	content of mercaptan sulphur initial	content of mercaptan sulphur in purified fraction
Straight-run petrols	50—150	$Fe(CO)_5$	18	7	6.5	0.3
	80—140	$(C_5H_5)_2Ni$	43	9	8.4	0.2
	50—150	$(Et\cdot C_6H_5)_2Cr$	35	8	7.1	1.0
Kerosines	145—230	$Fe_3(CO)_{12}$	170	8.7	6.0	0.4
	145—230	$CO_2(CO)_8Mn(CO)_6$	450	170	10	0.5
	120—226	$[C_5H_5W(CO)_3]_2$	160	40	48	0.05
	140—230	$Fe(CO)_4$ CH—CO ‖ >O CH—CO	230	90	21	0.7
Diesel fuels	187—355	$Fe_3(CO)_{12}$	1040	380	7.6	1.0
	200—380	$[C_5H_5Co(Co)_2]_2$	1420	630	9.0	0.2
	195—370	$C_6H_8Fe(CO)_3$	1200	270	10	0.5
Kerosines*	—	$Fe_3(CO)_{12}$	175	160	16	2.4
		»	170	90	6.6	0.3
Straight-run mazut	—	$Fe_3(CO)_{12}$	560	200	—	—

*Kerosines from pilot plant.

The formation in these processes of cluster compounds of the heteroatomic components of petroleum and some of their reactions, leading to the regeneration of the mercaptans and the formation of some of their derivatives, have been reported[61]. The elimination of heteroatomic compounds by the complexes investigated is apparently accompanied by a significant entrainment of aromatic hydrocarbons[60], which is observed in all sorption and extraction processes leading to the formation of sulphide-aromatic concentrates, as stated above.

Plyusnin and coworkers[62-64] used complex formation with titanium tetrachloride for the isolation of tars, asphaltenes, and heteroatomic compounds from petroleum and petroleum fractions. Tars and asphaltenes were initially isolated from petroleum in a Soviet deposit (Tomsk region) by the method of Pozdyshev et al.[17] with the aid of methanol-acetone mixtures. This petroleum contained 2% of asphaltene, 6% of silica gel tars, 0.85% of total sulphur, and 0.19% total nitrogen (0.064% of basic nitrogen). Model solutions of tars in n-hexane and of asphaltenes in benzene were investigated: a fractional precipitation was carried out by the stepwise addition of $TiCl_4$. Eight fractions of tar complexes were obtained for the consumption of between 1 and 5 moles of $TiCl_4$ per mole of tars and three fractions of asphaltene complexes for the consumption of between 7 and 10 moles of $TiCl_4$ per mole of asphaltenes.

The degree of extraction of tars was about 95% and that of asphaltene about 99%. In view of this result, the authors[62] carried out experiments on petroleum without preliminary isolation of tars and asphaltenes. A change in the weight ratio of $TiCl_4$ to petroleum from 0.008 to 0.054 made it possible to observe the characteristics of the precipitation of the petroleum components. After the addition of 0.020 $TiCl_4$ (by weight), the asphaltenes are isolated completely, almost in proportion to the amount of added $TiCl_4$. For the complete extraction of tars, its weight fraction should be at least 0.050 of the petroleum taken. The curve describing the isolation of tars as a function of the amount of $TiCl_4$ is S-shaped with a linear section in the range 0.010–0.030 $TiCl_4$. Low-molecular-weight heteroatomic petroleum compounds, coprecipitated with asphaltenes and tars in amounts comparable to the latter, are isolated in an unusual manner. They are clearly distributed in two groups separated by a region where their isolation is not observed. This region coincides with the linear section of the tar isolation plot. It is interesting that the concentrates isolated in the presence of small amounts of added $TiCl_4$ (0.003) contain 62% of low-molecular-weight heteroatomic components, 25% of asphaltenes, and 13% of tars. Following the addition of 0.030 $TiCl_4$, a concentrate was obtained where the fractions of the same groups were 30%, 20%, and 50% respectively. The complexes of low-molecular-weight HAC with $TiCl_4$ are hydrolysed much more readily than the complexes of tars and asphaltenes, which permits their separation.

After the addition of 0.050 $TiCl_4$ to petroleum from a Soviet deposit in the Irkutsk region, more than 99% of the additive was bound in a complex. Together with tars and asphaltenes, $TiCl_4$ binds 80–95% of the nitrogen in petroleum (100% of basic nitrogen) and about 60% of sulphur. These results were used to isolate HAC concentrates of distillates. Their isolation from the 140–240°C fraction of Western Siberian petroleums, processed at the Omsk refinery, has been investigated[63]. The yield of the HAC isolated was 0.25% and their composition was as follows: 67.6% C, 14.0% H, 7.6% S, 0.9% N, and 9.9% O (by difference) (M = 172). The entire nitrogen and neutral oxygen were concentrated in tar-like fractions obtained on chromatography of the HAC (after the elimination of the acid components with 10% NaOH solution) on silicic acid. Sulphur is mainly contained in higher thiacyclanes (and possibly thiophens). Neutral oxygen is present in ketones and acid oxygen in phenols. Basic nitrogen can also be fully eliminated by $TiCl_4$ from higher-boiling fractions[64]. A considerable proportion of the sulphur and oxygen compounds are extracted at the same time, as can be seen from Table 3. The average composition of the concentrates from petroleum in the Tyumen deposit corresponds to 40–50% of sulphur compounds, 2% of carboxylic acids, 1% of ketones, and 5–9% of nitrogen compounds. Using $TiCl_4$, 98% of basic nitrogen was extracted from vacuum gas oil (340–500°C fraction) (6.8% of the concentrate containing 0.042% of basic nitrogen and 1.5% of total sulphur was obtained).

Table 3. Elemental composition of the concentrates isolated from fractions of Tyumen petroleums at the Omsk refinery (in wt.%).

Fraction, °C	C	H	S	N	O	–COOH	$>$CO*
300–325	81.21	11.18	5.0	0.3	2.3	0.35	0.11
325–350	—	—	4.2	0.2	—	0.22	0.05
350–375	81.62	12.07	4.4	0.4	1.5	0.34	0.08
375–400	78.39	11.74	5.5	0.3	4.0	0.26	0.12

*The method used to determine the carbonyl groups has been described by Maikova et al.[65]

The data considered above suggest that there are good prospects for further improvement in the methods for the differentiation of the heteroatomic components of petroleum into subgroups, particularly in relation to heavy and residual fractions, with the aid of variable-valence metal salts.

The use of complex formation and ligand exchange for the isolation and separation of the HAC is only just beginning to develop. At the present time we know much more about the extraction of metals by organosulphur compounds than about the separation of sulphur compounds by metal salts. The use of $FeCl_3$ on clay had been described previously[67].

Starting from 1973[66], groups of research workers of the American Petroleum Institute and the Bureau of Mines, investigating the composition of heavy petroleum fractions, freed the crude material from the acid and basic components with the aid of anion and cation exchangers and then extracted neutral nitrogen compounds with iron(III) chloride.

The development of ion-exchange methods (their acid–base versions were described above) led to the creation of ion-exchange resins, zeolites, and a number of amphoteric oxide sorbents in salt-forms. In these sorbents, hydrogen ions have been replaced by metals: Na, K, Mg, Ca, and, especially, the variable-valence metals Cu, Fe, Co, Ni, etc.

III. CHROMATOGRAPHIC AND MASS SPECTROMETRIC METHODS FOR CHARACTERISING THE SULPHUR COMPOUNDS IN PETROLEUM AND ITS FRACTIONS

The commercial manufacture of satisfactory and continuously improved apparatus for different types of chromatography as well as the expansion of the range of stationary and mobile phases for chromatography have led to an appreciable increase of the efficiency of separation of multicomponent systems, particularly petroleum and petroleum products containing heteroatomic compounds of different types. The number of papers, reviews, and monographs devoted to chromatographic methods is very large and we shall describe selectively only some of them.

As already stated, most of the heteroatomic petroleum compounds have been found in higher petroleum fractions. The use of anion-exchange resins, described above, has been recommended for their isolation. Versions of liquid chromatography using ion-exchange resins have been developing in recent years. Thus the study mentioned above[66] was preceded by a methodological investigation of Haynes and coworkers[68], including chromatographic procedures for the separation of the heavy part of petroleum into acids, bases, and neutral nitrogen compounds. In 1975 Vogh and Dooley[68] suggested that the copper-form of the carboxylic acid cation-exchange resin *Bio-Rex*-70 be used. Attention has been concentrated on the shrinking of the copper-saturated cation exchanger during preparation (it amounts to 10–20% along the column length). Both in model systems and in heavy petroleum fractions containing mono-, bi-, and polyaromatic components with a mixture of polar compounds, virtually complete extraction of sulphides, was achieved. Ben'kovskii and coworkers justly regard Vogh and Dooley as their predecessors[54]. However, a detailed study of the sorption of sulphur and nitrogen compounds and the static and dynamic capacities of KU-2 cation-exchange resin in metallic forms (silver, copper, mercury, lead) and AV-17-4 and AV-17-8 anion-exchange resins were not reported until later[69]. In this investigation, Ben'kovskii et al. studied the sorption of a number of mercaptans from benzene and alcoholic solutions and demonstrated the possibility of the extraction of certain individual nitrogen compounds by cation exchangers in metallic forms. Useful information concerning the separation of anion-exchange resins for the chromatography of high-boiling petroleum fractions has been published[70].

Particular attention must be concentrated on the use of liquid chromatographic methods under high and moderate pressures, whereby one can significantly reduce the diameter of the sorbent particles used, i.e. one can greatly enlarge the area of the interface and one can increase by several orders of magnitude the rate and efficiency of the separation. This method is described in greater detail by Zhukhovitskii[71] and Kirkland[72]. Bezinger succeeded in dissolving the nitrogen concentrates from petroleum in the Novo-Dmitrovsk deposit into distinct fractions in approximately 2 h using the technique developed in Chumakov's laboratory. A similar separation could not be achieved previously even after passage through a chromatographic column over a period of two months (without the application of pressure). Studies by Cook and Spangelo[73] on the separation of phenols and by Janini et al.[74] on the separation of polyaromatic hydrocarbons have shown that research on the application of liquid-crystal (nematic) phases in the gas–liquid chromatography (GLC) of heteroatomic compounds of petroleum merits attention; this has been confirmed[75]. An interesting method has been proposed by Rudenko and Ryashentseva[76] for the identification of peaks of the GLC chromatograms of multicomponent mixtures with the aid of ray diagrams; correction coefficients for a number of compounds by a procedure put forward previously were determined at the same time[77]. Postnov et al.[78] examined an internal calibration method taking into account the necessary corrections for quantitative GLC analysis. These procedures can be used successfully in the GLC analysis of heteroatomic compounds and the petroleum fractions containing them.

A GLC analytical method without a standard, using several stationary liquid phases at different temperatures, was proposed by Golovnya and Arsen'ev[79] for the homologous series of mercaptans, sulphides, and disulphides. This investigation is a continuation of previous studies[80-82]. In order to elucidate the applicability of the approach developed by the authors to more complex systems of compounds, typical for petroleum and its derivatives, much additional research is needed.

Gusinskaya and Beiko[83] investigated the catalytic microdesulphurisation of the 140–220°C fraction of the petroleum from the Kokaity deposit in Southern Uzbekistin. Using a distribution tap, the microdesulphurisation unit was included between two chromatographs. The sulphides were separated on the first chromatograph, with a katharometer, in accordance with the chromatographic peaks and passed to a microreactor, whence the sulphide conversion products formed were transferred to the second chromatograph with a flame-ionisation detector. The best catalyst for desulphurisation proved to be the industrial AP-56 catalyst. Experiments with individual sulphides showed that hydrodesulphurisation in the presence of this catalyst yields pure hydrocarbons with the appropriate composition and structure, uncontaminated by their isomerisation or decomposition products.

Gas–liquid chromatography is at present the most rapid method for the investigation of the compositions of petrols in terms of individual compounds. For each group of organosulphur compounds (mercaptans, sulphides, and thiophenes), the number of isomers boiling in the same temperature range greatly exceeds the number of isomeric hydrocarbons having the corresponding structure. This hinders analysis for two reasons: (1) the relative concentrations of the components in the sulphur-containing fraction of petrol are much lower than the concentrations of hydrocarbons in its hydrocarbon fraction; (2) the synthesis of model sulphur compounds, which are very necessary for the labelling and interpretation of the chromatograms, is very difficult and the solution of this problem is virtually impossible for the majority of laboratories. Together with Gordadze and Gollandskikh, the author of the present review[84,85] achieved the photochemical methylenation of a number of individual thiaalkanes and thiacyclanes. It was shown that the methylene group, obtained on decomposition of diazomethane, is inserted in all the C–H bonds of sulphides. The reaction is not complicated by side processes and its course is just as rigorously statistical as with hydrocarbons[86]. The observed slight deviations towards reduced reactivities of the C–H bonds at the carbon atoms adjoining the sulphur atom play hardly any role. Individual methylenated sulphides can be fully recommended as standards for the GLC analysis of sulphide-containing fractions. For a description of the application of GLC analysis in petrochemistry, see Refs. 87–89.

Drushel[90] recommended an unusual version of the reactochromatographic analysis of the sulphide–thiophen fraction of organosulphur compounds in petroleums as a more rapid method for the determination of the group composition of such compounds. The test specimen (in a stream of nitrogen or helium) is introduced into the chromatograph via a micropyrolytic cell (at 790°C in pyrolysis and at 600°C in the presence of Al_2O_3; benzothiophens are dealkylated in this cell and sulphides form hydrogen sulphide and, partly, mercaptans. The mixture of products, separated in the chromatograph, is transferred to a combustion tube, where oxygen is supplied (apart from the nitrogen or helium carrier gas) ($t \simeq 850$°C). The hydrogen sulphide formed passes to a microcoulometric (iodometric) cell connected to a pen recorder, which records the integral current–time curve. We do not know how much this method is used. It makes it possible to differentiate the sulphur in heavy petroleum products into the components present in aliphatic sulphides or "non-thiophens", benzothiophens, dibenzothiophens, benzonaphthothiophens, and unknown sulphur compounds. The duration of the experiment is approximately 1 h and the accuracy is to within 2–3%. The results agree well with those obtained previously by the mass-spectrometric method[91].

A novel "centri-chromatographic" method, combined with mass-spectrometry, has been proposed by Canadian investigators[92] for the separation of small amounts of multicomponent systems. The fundamental principle of centrifugal chromatography is similar to that of liquid chromatography under pressure. The method has apparently not found applications as yet in the study of petroleums and petroleum products. Drum thin-layer chromatography, used by Sanders and Snyder[93] is of interest. The application of thin-layer chromatography to organosulphur compounds has been examined by Karaulova[94].

Gel chromatography has been recommended as a useful subsidiary method for the separation of petroleum components[95,96]. This type of chromatography has been incorporated as the final stage in the multistage schemes for the separation of petroleums, adopted by the American Petroleum Institute and the U.S. Bureau of Mines, which were described above[66,67]. These studies were preceded by the careful investigation of Coleman et al.[99] of the use of gel permeation chromatography in relation to high-boiling petroleum components.

The characteristics of the composition of the petroleum fractions obtained by different methods and the determination of the structure of their components can be achieved on the basis of the chromatographic analysis only of the most low-boiling fractions. Higher-boiling fractions require additional chemical and physical research techniques. Among the latter, mass-spectrometry has proved to be the most informative at the present time. Some of the versions of mass-spectrometry can be combined with chromatography in integral chromato-mass-spectrometric apparatus operating particularly efficiently in combination with integrating computing devices.

There is insufficient space in the present review to consider the advances in the instrumental and computing techniques associated with the development of chromatography and mass-spectrometry. Nevertheless some of the relevant investigations must be mentioned. Robinson and Cook[100] examined in detail the application of low-resolution mass-spectrometry in the study of the group composition of the aromatic fractions of petroleum and were able to identify in the latter three main groups of compounds, each of which was in turn subdivided into seven subgroups. These consisted of dibenzofurans and benzo-, dibenzo-, and benzonaphtho-thiophens. Severin et al.[101] investigated the application of 10 eV mass-spectrometry combined with field ionisation to higher petroleum fractions. Anbar and Aberth[102] recently re-examined in detail mass-spectrometry with field ionisation in relation to vacuum distillates (176–360°). They used an apparatus with multichannel recording and automatic integration. They believe that the principal advantage of the method is a reduction of the degree of decomposition, which simplifies the spectra of the components, this being particularly important for the analysis of multicomponent systems. Problems concerning the use of mass-spectrometry with field ionisation in the study of labelled substances have been examined by many investigators; errors due to isotopic effects and fragmentation artifacts are then eliminated. The method has been recommended for the investigation of biogenic systems of complex composition. This may well prove extremely useful in the study of the heteroatomic components of the heavy part of petroleum, bitumens, and the organic material in the deposits in the existing seas and lakes.

Certain considerations favouring the use of cyclotron mass-spectrometry in the analysis of substances with ultralow vapour pressures have been described in a recent study[103]. After appropriate development, the new method will assist in the investigation of tar and asphaltene fractions of petroleum in which the majority of heteroatomic components are concentrated. Gallegos et al.[104] described in detail high-resolution chromato-mass-spectrometric analysis using as an example a study of pyrolysis products (the presence of 152 hydrocarbons, 8 cyclic and 5 acyclic dienes, and 18 unidentified compounds in such products was established).

Brodskii and coworkers[105-107] and Khmel'nitskii[108] obtained a number of new data concerning the characteristics of individual heteroatomic compounds, primarily sulphides[105-108]. Brodskii et al.[109] described the mass-spectrometric analysis of aromatic hydrocarbons and sulphur compounds present jointly in petroleum fractions; their distribution in 23 groups based on the C_nH_{2n-x} and $C_nH_{2n-y}S$ homologous series with the even values $x = 6–24$ and $y = 4–22$ is described and the relative ionisation cross-sections of the compounds are given. Khmel'nitskii et al.[110] described the mass-spectrometric analysis of nitrogen-containing bases in petroleum having the composition $C_nH_{2n-z}N$ with the odd values $z = 9$, 11, and 13.

A general examination of the principles of the mass-spectrometric investigation of heterocyclic nitrogen compounds has been made in Klyuev's dissertation[111]. The mass-spectrometric analysis of nitrogen and sulphur compounds based on fragment ions has been used[112] to investigate the petroleums from the Tajik depression (Southern Uzdekistan). An analytical method based on molecular ions was developed in that investigation for sulphur compounds whose molecular weights range from 350 to 600, involving their subdivision into seven groups differing in the degree of unsaturation with respect to hydrogen. Mal'tseva's study was devoted to an examination of the mass spectra of bicyclic heterocyclic compounds[113]. Popov developed methods for the mass-spectrometric and chromato-mass-spectrometric analysis of nitrogen-containing bases in mineral fuels[114]. Such comparative studies are of undoubted interest, since latest investigations[115] have demonstrated a similarity of the composition of the products obtained from coal by mild modern procedures to the composition of the heavy components of petroleum.

Brodskii et al.[116] emphasised that, in an investigation of the composition of complex products such as petroleum distillates, data obtained by previously developed simpler methods are useful in addition to results obtained by chromatography and mass-spectrometry. Comparison of the data derived by the two groups of methods makes it possible to improve significantly the assessment of the structural-group compositions and structures of the products investigated. The development of mass-spectrometry in combination with detailed correlations for the analysis of the heteroatomic components of petroleums, coals, shales, and the products of their processing has been described by Brodskii[117].

Polyakova et al.[118] examined the possibility of using high-resolution mass-spectrometry for the investigation and quantitative determination of thiacyclane and thiophen derivatives with different numbers of rings. Petroleum fractions have been analysed in the 400–650 mass range with the aid of the spectrometry of mass defects. The authors[118] developed a novel system for the calculation of the composition of the multiplets and compiled tables of the molecular weights of ions for a series of compounds in the residual petroleum fractions.

A number of monographs, for example that of Polyakova and Khmel'nitskii[119], have been devoted to mass-spectrometry in recent years. These methods need not therefore be considered further. Interesting information about the structure and properties of the heteroatomic components of petroleums can be obtained by the application of proton magnetic resonance. Unfortunately it has not so far been adequately developed, despite the fact that Clutter et al.[120] pointed out as early as 1972 the likelihood that a method can be devised for group NMR analysis, similar to the mass-spectrometric group analytical techniques. At the same time, NMR has been used[121] to determine the content of acids and bases in organic substances. The proton magnetic resonance method has been employed[122-124] in the study of the structural-group characteristics of the nitrogen-containing bases in Sakhalin petroleums. ^1H NMR yielded valuable information about the admixture of oxygen compounds with a furan ring in nitrogen-containing bases (the presence of diaryl ethers is not ruled out)[122] and about the ring sequence in tricyclic systems, demonstrating that angular junctions in the latter are more probable than *peri*-junctions.

Presumably ^1H NMR combined with modern computing-analytical devices will take its due place in research on petroleum products in the immediate future. The information about the homology and the number of rings present yielded by mass spectrometry will then be supplemented by the characteristics of the location and mobility of hydrogen atoms, which are directly related to the reactivity of petroleum components.

IV. PETROLEUM SULPHIDES AND THIOPHENS

In 1966 Smith[125] published a novel and elegant review of the available information concerning the qualitative and quantitative composition of crude petroleum. He recognised for the first time the quantitative equivalence of the hydrocarbon and non-hydrocarbon components of petroleum. However, the available information about the heteroatomic compounds of petroleum, particularly the high-boiling compounds, was inadequate for the determination of the correct proportions of the individual groups. A detailed survey of studies on Project 48A of the American Petroleum Institute carried out during the 20 years from 1948 to 1968 was made by a group of investigators under Thompson's supervision[126]. The group composition of the sulphur compounds in the vacuum distillates from petroleums in 17 deposits was first investigated. Determinations were made of the contents of (1) free sulphur, (2) hydrogen sulphide, (3) disulphides,

(4) mercaptans, (5) and (6) two groups of sulphides, and (7) "residual sulphur" using Ball's method[127] and it was stated that this procedure yields distorted data owing to the coprecipitation of the components when they are removed by group reagents (for further details about this, see Luk'yanitsa[128]). As a result, it was established that, for a monotonically increasing sulphur content in vacuum distillates, the qualitative compositions of sulphur compounds in the latter remain similar but the quantitative proportions of the groups vary sharply, being uncorrelated either with overall sulphur content in the petroleum or with its contents in the distillate. The distillates from the Goldsmith petroleum, where the content of free sulphur reaches 42.5% and the Deep River petroleum, where the content of mercaptans is 46%, are unique. The fraction of sulphides in the Velma petroleum is 42%. The maximum residual sulphur (80%) has been observed in the distillate from Heidelberg petroleum. The Wasson petroleum (Texas) was selected as the main object of study. The following components were identified in its fractions boiling up to 250°C as a result of the application of multistage separation schemes, chromatography, complex formation, mass spectrometry, etc: 47 mercaptans (including six alicyclic mercaptans and one aromatic mercaptan); 38 dialkyl sulphides; 5 alkyl cycloalkyl sulphides; 4 alkyl aryl sulphides; 21 thiacyclanes; 18 thiaindans; 2 disulphides; 22 benzothiophens; 2 dibenzothiophens; 160 compounds in all. However, alkylthiophens were not found (11 examples of this series were discovered in Wilmington petroleum). Quantitative estimates of the contents of 44 individual compounds were made. 58 papers were published on Project 48A during the period under consideration; some of these data are considered in Karaulova's monograph[129].

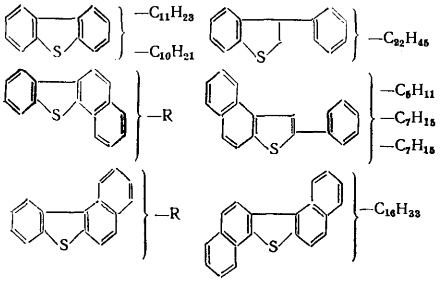
During the same period, detailed studies were made by Obolentsev and coworkers[130-133] and Vyakhirev et al.[134] on the organosulphur compounds present in the petroleums of the Urals-Volga petroleum-bearing region. The presence of mercaptans and a large number of sulphides was established in these petroleums. Among the sulphides, thia-alkanes are concentrated in the light fractions and thiacyclanes in the heavy fractions. Thiophen and methyl- and dimethyl-thiophens were identified in Romashkino petroleum[134]. These studies have been reviewed by Krivolapov[135] and Allilueva[136]. The GLC retention parameters of a number of sulphides have been calculated in the latter review.

Beiko and Gusinskaya[137] continued the investigation of the boiling points and the retention parameters of isomeric thiacyclanes. These data enabled Beiko[138] to investigate the composition of the petrol-kerosine distillates from petroleum in the Kokaity deposit. The results agree well with a series of studies devoted to the investigation of the middle fractions of petroleum from Southern Uzbekistan (the Tajik depression). A more detailed investigation of the 200–400°C fraction of combined Southern Uzbekistan petroleums (from Khaudape, Lyal'mikar, and Kokaity deposits) was made by the present author and his coworkers[139,140]‡ and in the course of this study numerous techniques were improved. The sulphides of the individual Khaudag and Kyzyl-Tumshuk petroleums were studied (simultaneously with the present author's research) at the Institute of Chemistry of the Academy of Sciences of Tajik SSR[142]. The petroleums from the Kokaity and Lyal'mikar deposits have been reinvestigated in Tashkent[143]. A mass-spectrometric investigation[112] was mentioned in the preceding Section. This was the first study to include the heavier components of the petroleums from the Tajik depression (Southern Uzbekistan). Some of the relevant data have been examined in monographs[129,144,145]. Here one must emphasise that the qualitative compositions of the petroleums from different deposits in the Tajik depression of Southern Uzbekistan are similar. This phenomenon has been known for a long time for petroleum hydrocarbons. The organosulphur compounds have been found to be similar as a result of research in recent years.

The petroleums of Southern Uzbekistan are characterised by negligible contents of light fractions and an almost complete absence of mercaptans and disulphides. The sulphides of the 200–400°C fraction consist mainly of a series of thiacyclanes[139] containing between 1 and 5 rings. Thiamonocyclanes (60%) containing between 7 and 21 carbon atoms per molecule predominate. Thiophens in this fraction also include series of compounds containing between 1 and 4 rings. The main bulk consists of benzothiophen (~33%) and condensed cycloalkyl- and dicycloalkylbenzothiophens (approximately 21% of each). The content of alkylthiophens (about 16%) is fairly high.

In terms of the order of magnitude, the values found in later studies for petroleums of Southern Uzbekistan[112,143] are close to those obtained by the present author[139]. The differences in the selection of fractions and in the details of the methods employed preclude a comparison of the quantitative data obtained in the three investigations or an estimate of the fine differences between the component compositions of the sulphur compounds in individual petroleums. The differences between the contents of thiaindans in the petroleums from different deposits in this region are significant: Kyzyl-Tumshuk—12%; Khaudag—9%; Dzhar-Kurgan—1-4%[112]; Lyal'mikar—3.3%; Kokaity—5%[143]; a mixture of Khaudag, Lyal'mikar, and Kokaity petroleums—4.5%.[139] If these data are confirmed, then the petroleum from the Kyzyl-Tumshuk deposit must be collected separately, particularly for the isolation of thiaindans, which are of special interest.

After the extraction of nitrogen compounds, it was established mass-spectrometrically in conjunction with infrared spectroscopy[112] that petroleum from the Dzhar-Kurgan deposit (150–350°C fraction) contains complex benzothiophen compounds, whose probable structure can be represented by the following formulae:



,

where R = $C_{19}H_{39}$, $C_{21}H_{43}$, and $C_{23}H_{47}$. Gal'pern et al.[146] investigated the structural-group composition of the sulphur-containing concentrate from the 350–370°C oil distillate of petroleum from the Romashkino deposit. The C_{21}–C_{24} fraction with 6.00% S_{tot}, 2.00% S_{R_2S}, and n_d^{20} = 1.4643 was isolated by chromatography on silica gel. Oxidation with hydrogen peroxide and subsequent regeneration (by reduction with lithium tetrahydroaluminate)

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‡These data have been examined in detail in a compilation published quite recently[208].

yielded, by a procedure similar to that used in another study[139], sulphides formed from sulphoxides (obtained by oxidation with hydrogen peroxide in acetic acid and acetic anhydride and residual sulphoxides). A decrease of selectivity relative to that observed in the oxidation of lower-boiling distillates in acetic acid was observed: there is a significant increase of the fraction of thiophen compounds in the oxidation products. On reoxidation in acetic anhydride, alkyl aryl sulphides and thiaindans are fully converted to oxidation products. The total sulphides obtained by two-stage oxidation exceeds the sum of the sulphides obtained in single-stage oxidation (directly in acetic anhydride). If the oxidation is restricted to the first stage only (with acetic acid), all the saturated sulphides are fully converted into sulphoxides, but the majority of thiaindans and aryl sulphides remain in the refined products. The sulphides obtained were analysed mass-spectrometrically. Altogether 14% of sulphides and 55% of thiophens were found in the fractions; their distribution among subgroups is described by Gal'pern et al.[146]

Sulphides in the petroleum from the Arlansk [tentative transcription] deposit were isolated from the 170–310°C fraction[147]. Their purification and re-extraction by sulphuric acid was completed by a mass-spectrometric study of the composition of the concentrates[148] obtained by treatment with 86% sulphuric acid, subsequent extraction with 91% acid, and chromatographic separation into narrow fractions.

A series of fundamental studies on the compositions and structures of the sulphides in the kerosene and gas oil fractions of Arlansk petroleum have been carried out by Nikitina and coworkers[52,149–151]. The average molecular weights of dialkyl sulphides and alkyl cycloalkyl sulphides are higher than those of thiamono- and thibi-cyclanes; the average molecular weight of benzothiophens is lower than the corresponding values for alkyl- and cycloalkyl-thiophens. It has been shown[55] that an increase of the concentration of sulphuric acid in the extraction of sulphide concentrates from petroleum distillates leads to an increase of the fraction of sulphides and thiaindenes extracted and to an appreciable decrease of the average molecular weights of all the components of the extracts. This phenomenon is probably associated with the enhancement of the hydrophobic properties of the sulphides with increase of their molecular weights and with decrease of the degree of dissociation of the monosolvates of the 'onium complexes of the sulphides with sulphuric acid when the concentration of the latter increases. Comparison of the compositions of the sulphides extracted from the Arlansk petroleum fractions with those of the corresponding sulphides of Romashkino and Southern Uzbekistan petroleums demonstrates their considerable similarity. The conclusion[27] that thia-alkanes and alkyl cycloalkyl sulphides are extracted in succession by dilute sulphuric acid has been disproved[55]. In the initial investigations, the mass-spectrometric technique was apparently inadequate for the determination of low concentrations of higher thia-alkanes characterised by a uniform mass distribution[208].

The experimental industrial apparatus for the preparation of sulphide concentrates from petroleum distillates has been described[153]. The Arlansk petroleum concentrates obtained[154] were investigated by the formation of complexes with $AgNO_3$ and with thiourea, this being followed by thermal diffusion fractionation and mass-spectrometric analysis. The low efficiency of the formation of adducts with thiourea by sulphides from the middle fractions of petroleums as regards their differentiation into structurally different groups was demonstrated in this investigation. Thermal diffusion makes it possible to reduce the concentration of polycyclic sulphides and to concentrate them in the last fractions. In view of the low efficiency of the method, one can hardly hope for extensive application of the thermal diffusion of sulphides. In this sense, the employment of gas–liquid chromatography under increased pressures is much more effective. It has been shown[154] that thiamonocyclanes have on average three alkyl substituents and thiabicyclanes have two substituents, only one of these with a long chain containing between 2 and 8 carbon atoms. The distribution of the sulphide subgroups with respect to mass is largely determined by the chain length. These results are fully consistent with those obtained earlier[140,208] for the corresponding sulphides from the distillate of Southern Uzbekistan petroleum.

The latest studies on the sulphides in Western Siberian petroleums (from the Western Surgut and Samotlorsk [tentative transcription] deposits[30,31,154,155]) confirm the hypothesis that the compositions of the sulphides in mercaptan-free petroleums are similar. Data for Arlansk, Western Surgut, and Samotlorsk petroleums, obtained in the same way and investigated by the same procedures, have been compared[155]. In all the 190–360°C distillates, the fraction of thiacyclanes is 85–90% of the total sulphides. The relative contents of mono-, bi-, and poly-thiacyclanes vary in the ranges 50–58%, 20–23%, and 9–14% respectively. The concentrates contain alkyl-, cycloalkyl-, benzo-, and dibenzo-thiophens and condensed naphthenobenzothiophens. Their relative concentrations for Samotlorsk petroleum (with a lower total of sulphur content) distinguish the latter from the high-sulphur petroleums, particularly from the Southern Uzbekistan and Arlansk petroleums discussed above.

A series of studies by Thompson and coworkers have been devoted to the high-boiling fractions of five individual petroleums[157–161]. A brief description of these investigations has been published[162–166] and their overall resumé can be found in the paper by Dooley et al.[167]. Acid and basic components have been extracted from distillates by liquid chromatography under pressure with the aid of Amberlyst A-29 anion-exchange resin and Amberlyst A-15 cation-exchange resin respectively, while iron(III) chloride has been used to extract neutral nitrogen compounds (after a preliminary elimination from crude petroleum of solid paraffins which were subjected to separate mass-spectrometric analysis). Distillates freed from the above compounds were analysed and subjected to preparative liquid chromatography on silica–alumina gel for separation into four fractions: saturated and mono-, di-, and poly-aromatic compounds. The fractions of saturated compounds were transferred directly to mass-spectrometric analysis and the aromatic fractions were analysed mass-spectrometrically after an additional gel-chromatographic separation. Table 4 presents data characterising the yields and compositions of the distillates, refined products, and seven fractions. Evidently the main bulk of sulphur is concentrated together with the di- and poly-aromatic compounds. Anion-exchange resins, cation-exchange resins, and iron(III) chloride extract from 370–535°C distillates about 5% of the compounds (California petroleum yielding up to 16.5% is an exception). All three sorbents extract also neutral sulphur compounds, in most cases in amounts comparable to those of the nitrogen compounds. The comparatively high concentration of sulphur in these extraction fractions does not play a

Table 4. The yields* of 370–535°C distillates, their chromatographic fractions, and their elemental compositions (wt.%) (based on the data of Dooley et al.[167]).

Initial Petroleum	Yield and composition of distillate	Extracted			Yield and composition of refined product	Paraffin-naphthene fractions	Monoaromatic fractions	Diaromatic fractions	Polyaromatic fractions HAC
		by anion exchanger	by cation exchanger	by $FeCl_3$					
Prudhoe Bag (Alaska)	21.630a	2.840d	2.460d	0.900d	93.800d	48.310d	16.98d	11.910d	16.600d
	0.191b	2.346b	2.935b	2.095b	0.080b	0.014b	0.010b	0.025b	0.210b
	0.170c	0.940c	2.590c	2.050c	1.130c	0.080c	0.100c	2.520c	3.920c
Gach Saran (Iran)	19.670a	1.710d	2.120d	1.170d	95.000d	48.490d	16.830d	11.700d	17.980d
	0.223b	2.290b	3.498b	2.577b	0.083b	0.013b	0.013b	0.027b	0.320b
	1.850c	1.602c	2.380c	3.490c	1.940c	0.080c	1.040c	3.910c	5.920c
Swan Hills (Canada)	18.350a	1.770d	2.190d	0.460d	95.580d	65.940d	12.550d	6.270d	10.820d
	0.147b	2.641b	2.799b	3.716b	0.034b	0.018b	0.027b	0.025b	0.231b
	0.280c	0.730c	1.850c	3.460c	0.240c	0.010c	0.100c	0.700c	1.830c
Wilmington (USA)	24.690a	5.580d	6.770d	4.230d	88.410d	36.910d	16.810d	12.360d	17.330d
	0.458b	1.407b	3.329b	2.592b	0.071b	0.007b	0.017b	0.007b	0.288b
	1.580c	1.400c	1.230c	1.740c	1.600c	0.090c	1.020c	2.810c	4.600c
Recluse (USA)	18.580a	1.350d	1.150d	0.930d	96.570d	74.120d	11.270d	5.060d	6.120d
	0.069b	1.569b	2.229b	2.640b	0.043b	0.010b	0.001b	—	0.100b
	0.120c	0.410c	0.120c	2.190c	0.220c	0.040c	0.100c	0.490c	2.020c

* a—yield with respect to petroleum; d—yield with respect to distillates; b—nitrogen content; c—sulphur content in products a and d.

significant role in the overall sulphur balance, since their yield is low. The study of sulphur-containing components of extracts is difficult and so far is not susceptible to interpretation by mass-spectrometric methods. They probably contain a large amount of compounds, each with two and more heteroatoms per molecule (including oxygen atoms), at fairly high concentrations. This distinguishes them from the main bulk of the monofunctional organosulphur compounds transferred together with the paraffin-naphthene fractions and makes them similar to the polar polyaromatic concentrates.

The nitrogen and sulphur contents in the paraffin-naphthene fraction is low, but, despite the low concentrations of the corresponding heteroatomic compounds, one must not forget that the proportion of these saturated fractions is usually between 37 and 74% of the initial distillates. A comparatively monotonic decrease of the yields of the groups of hydrocarbons from 41 to 25% with increase of the number of rings in the latter from zero to 6 is characteristic of such distillates. In the series of petroleums considered, Wilmington petroleum is an exception, its saturated fraction containing only 13.5% of alkanes, 15.8% of monocyclanes, and 14.0% of bicyclanes; the content of tricyclanes is somewhat higher (15.8%) and there is an unusual maximum corresponding to the proportion of tetracyclanes (25.9%). The content of pentacyclanes is 9.2%, which greatly exceeds the average for remaining types of petroleum (6%). There are as yet no data concerning the nature of the sulphur compounds remaining in the saturated paraffin-naphthene part of the refined product.

The distribution of the main groups of compounds among the aromatic fractions is given in Table 5, which shows that the sulphides and thiophens in the petroleums investigated are concentrated mainly in the polyaromatic compound fractions. The contents of individual groups of organosulphur compounds are distinguished by a great variety. The differences between their overall contents are very great: from approximately 20% in Recluse petroleum to nearly 100% in Gach Saran petroleum. The aromatic fractions include the hitherto undeterminable heteroatomic oxygen and nitrogen compounds. The Gach Saran petroleum contains a relatively large amount of components with more than one sulphur atom per molecule, which reduces the accuracy of the quantitative estimate of its overall content of organosulphur compounds. The differences between the qualitative compositions of the subgroups of compounds discovered in the five distillates investigated are even greater than the differences between their overall contents.

Table 5. The distribution of sulphides (S), thiophens (T), and aromatic sulphur compounds with unknown structure (A) in 370–535°C distillates (in wt.%) among chromatographic fractions (according to the data of Dooley et al.[167]).

Initial petroleum	Groups of compounds	Monoaromatic fractions	Diaromatic fractions	Polyaromatic fractions + HAC	Sums of S, T, and A
Prudhoe Bay (Alaska)	S	0.08	5.06	21.37	26,91
	T	2.31	21.34	14.42	38.07
	A	0.58	0.00	3.27	3.85
Gach Saran (Iran)	S	0.76	9.96	47.73	58.45
	T	6.95	31.23	21.07	59.25
	A	3.66	0.00	1.38	5.04
Swan Hills (Canada)	S	0 02	0.00	6.18	6.20
	T	2.05	5.07	14.80	21.92
	A	1.00	1.34	0.19	2.53
Wilmington (USA)	S	0.50	15.36	36.52	52.40
	T	6.10	19.70	16.73	42.53
	A	3.23	0.67	1.86	5.76
Recluse (USA)	S	3.54	0.00	0.00	3.54
	T	1.55	0.96	7.90	10.41
	A	0.00	4.24	2.66	6.90

Further investigation of the heteroatomic compounds in petroleums, in particular sulphides and thiophens, requires the development of chemical methods for their differentiation into subgroups. The differentiation of these compounds on the basis of their reactivity is not only of theoretical but also of great practical interest.

Comparison of the data of Soviet and foreign investigators clearly demonstrates fairly significant differences not only in the overall contents of sulphides and thiophens in petroleums from different deposits but also in their distribution among subgroups corresponding to different structures. Naturally, these differences must be taken into account in the utilisation of sulphides and thiophens as the raw materials for the chemical processing of petroleum.

V. OXIDATION OF PETROLEUM SULPHIDES

In the early stages of the research into the chemistry of the sulphides in the middle fractions of petroleum[168,169], the present author and his coworkers already demonstrated significant differences between the oxidation potentials of sulphides, other groups of sulphur compounds, and hydrocarbons, which made it possible to oxidise the sulphides to sulphoxides by hydrogen peroxide under mild conditions with a high degree of selectivity. The conversion of sulphides into sulphoxides alters sharply the polarity of the functional group. Sulphoxides, which are neutral under the usual conditions, behave as distinctly basic compounds in the oxidation products from petroleum distillates, which makes it possible to separate them readily from other groups of compounds both by chromatography on coarsely porous silica gels and by acid extraction[170,171]. The influence of the differentiating solvent (acetic anhydride) was investigated[172] in solutions of individual sulphides having different structures and compared with ethers in acetic acid. This established that the degree of oxidation of aromatic sulphides in acetic anhydride is three times as high as in acetic acid. The addition of perchloric acid sharply increases the rate of homogeneous oxidation of sulphides to sulphoxides in acetic anhydride.

The heterogeneous-emulsion oxidation of sulphides to sulphoxides in the presence of perchloric acid[173] made it possible to obtain sulphoxides in a single stage from distillates of sulphur-containing petroleums in which sulphoxide perchlorates are insoluble. The selectivity of the process then increases sharply owing to the acceleration of the main reaction. The process is applicable to the formation of individual sulphoxides from sulphides and to the purification, by reprecipitation, of the sulphoxides obtained by other methods. Here one should recall that the perchlorates of lower sulphoxides are explosive. The perchlorates of C_6 and higher sulphoxides are not quite so dangerous, but it is nevertheless recommended that they should be hydrolysed with water and aqueous solutions of alkali immediately after isolation, whereupon the resulting sulphoxides may be dried in the usual way.

The principal procedure for obtaining sulphoxides was believed to be the heterogeneous-emulsion oxidation of the sulphides present in petroleum fractions without their preliminary isolation or their isolation in the form of sulphur-containing aromatic concentrates. The method was first proposed by the present author[174] and was then elaborated in significantly greater detail and improved[175-178]. In the development of the appropriate technology, we selected foam reactors and obtained the sulphoxides under novel foam-emulsion conditions[179]. The technological development was carried out by Khitrik and coworkers[180,181] on laboratory and larger scales using a continuous-operation apparatus. The results obtained by Khitrik agreed very well with earlier data obtained by Bardina[177] on small laboratory periodic-operation devices. The Vitt bell stirrer used in these experiments created conditions close to foam-emulsion conditions. A separate experiment established that, under the conditions adopted, air always behaves as an inert gas without being involved in the reaction. The final development of the technology for obtaining sulphoxides from distillates and sulphur-containing aromatic concentrates was achieved on larger-scale continuous-operation apparatus (made of metal). The fundamental laboratory data found for the oxidation of phenolic and sulphuric acid extracts of the 275–350°C fraction of Arlansk petroleum by hydrogen peroxide under foam-emulsion conditions are presented in the report of Zagryatskaya et al.[182] The results largely agreed with those obtained previously on laboratory and large laboratory apparatus. The advantage of the sulphuric acid extracts of sulphides over the phenolic extracts was demonstrated. The selectivity of the oxidation process in the presence of catalytic amounts of acetic acid is higher than in the presence of sulphuric acid. Under foam-emulsion conditions, attention must be concentrated on the number of foaming steps, maintaining the appropriate size of the average cross-sections of the bubbles, which determine the overall areas of the liquid gas and liquid 1–liquid 2 interfaces.

Data on the kinetics of the oxidation of sulphides to sulphoxides in petroleum distillates by hydrogen peroxide under foam-emulsion conditions were published recently[183]. It was shown that the rate of the process can be expressed by the equation

$$V=1.42\cdot 10^7T^{1/2}\exp\left(-\frac{16200}{RT}\right)\cdot C_{R_2S}C_{H_2O_2}\ .$$

The order of the reaction with respect to the sulphide and hydrogen peroxide is unity, the overall order is two, and $\bar{E}$ = 16.2 kcal mole^{-1}. A significant proportion of the above studies are described in Khitrik's dissertation[184]; the studies of Masagutov et al. on pilot apparatus have also been published[209].

Experiments on the replacement of hydrogen peroxide by organic hydroperoxides in the presence of organic acids in reactions designed to obtain sulphoxides are noteworthy[185,186]. The degree of oxidation by isopropylphenyl hydroperoxide is higher by a factor of 1.5–2 than the degree of oxidation by t-pentyl and t-butyl hydroperoxides. The catalytic acceleration of the oxidation of sulphides is proportional to the strength of the carboxylic acids used.

It was natural to extend the oxidation of sulphides to sulphoxides to the next stage—the oxidation to sulphones. A test of the possibility of multistage and single-stage oxidation was of particular interest. The latter has been carried out for a long time and does not yield satisfactory results, because the sulphoxide → sulphone conversion is endothermic, in contrast to the exothermic sulphide → sulphoxide conversion. In the two-stage oxidation of petroleum distillates, one removes together with sulphoxides many impurities which char on vigorous oxidation. The refined product obtained contains hardly any sulphides or sulphoxides. On reoxidation, it gives a mixture of sulphones, among which predominate benzothienyl sulphones with an admixture of tricyclic sulphones belonging to different series (most probably dibenzothiophens, naphthothiophens, and naphtheno-, benzo-, and benzonaphtheno-thiophens).[187] The oxidation of saturated sulphoxides to sulphones is of considerable interest[188]. The authors found the optimum conditions for the oxidation of petroleum sulphoxide concentrates by hydrogen peroxide in the foam-emulsion state in the presence of catalytic amounts of sulphuric acid. The sulphoxide → sulphone conversion takes place to the extent of 95–96% in 15 min.

Petroleum sulphoxides are effective and promising extractants and floatation agents for the hydrometallurgy of non-ferrous and rare elements[189,210]. Nikitin et al.[190] reported the isolation and characterisation of 32 complexes formed by sulphoxides (obtained from the sulphuric acid concentrates of the 190–360°C sulphide fraction of Arlansk petroleum) with the nitrates and certain chlorides of magnesium, calcium, zinc, aluminium, chromium, iron, cobalt, nickel, manganese, bismuth, uranyl, and gallium. The bathochromic shift of the characteristic wavenumber of the sulphoxide group (ν = 1040 cm^{-1}) has been used to characterise the donor-acceptor bond in these complexes. $\Delta\nu$(SO) is a maximum for iron and chromium chloride complexes ($\Delta\nu$ = 95 cm^{-1}) and for the copper chloride complexes ($\Delta\nu$ = 90 cm^{-1}); among the nitrates, the maximum corresponds to chromium nitrate ($\Delta\nu$ = 110 cm^{-1}), nickel, bismuth, and uranyl nitrates ($\Delta\nu$ = 95 cm^{-1}), and copper nitrate ($\Delta\nu$ = 83 cm^{-1}). It was shown that, regardless of the method of preparation of the complexes, anhydrous solvates are isolated preferentially, with displacement of water from the coordination spheres of the ions and its substitution by sulphoxides. It is suggested that in some complexes sulphoxides are present in the inner and outer spheres, for example in $FeCl_3.3PSO$ (PSO = petroleum sulphoxide). The dependence of the extracting capacity of sulphoxides on their molecular structure has been examined[191]. It was shown that the extraction of metal salts by sulphoxides from aqueous solutions of hydrochloric, nitric, and sulphuric acids and from mixed media proceeds via hydrate-solvate and solvate mechanisms. The extraction of metals by sulphoxides from hydrochloric acid solutions has been discussed in detail[192]. It was shown for the first time in the same study that cyclic sulphoxides are extracted preferentially by uranyl nitrate from their mixtures with aliphatic sulphoxides.

Sulphoxides have been used[193] for the extraction-gravimetric determination of niobium and tantalum. It was shown that the determination is not interfered with by admixtures of magnesium, aluminium, copper, titanium, chromium, manganese, iron, cobalt, nickel, zirconium, molybdenum, tin, and lead over the entire concentration range.

Rafikov and Nikitin[194] examined the possibility of using sulphoxides and their metal salt complexes as the liquid phases in gas-liquid chromatography for the separation of saturated and unsaturated hydrocarbons. The complexes with $CuCl_2$ and $FeCl_3$ (charge-transfer complexes) were the most effective. Coloured organic glasses with improved heat resistance have been obtained on the basis of sulphoxide complexes with $MnCl_2$, $CoCl_2$, etc. added to poly(methyl methacrylates) and polystyrenes.

The extraction of organic acids by sulphoxides has been investigated and certain problems of their separation by extraction have been considered[195,196].

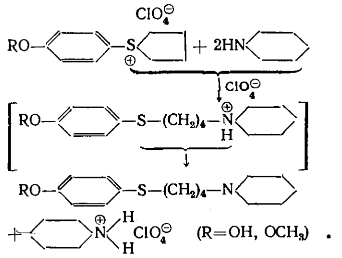
Apart from the direct utilisation of sulphides and sulphoxides in hydrometallurgy and in the chemistry of polymeric materials, it is also of interest to investigate in greater depth the chemical reactions of sulphides and sulphoxides originating from petroleum. In organic chemistry, the majority of these substances have so far been little studied or not at all. Such study required the simultaneous investigation of a number of reactions of individual compounds simulating the petroleum compounds.

The study[172] mentioned above, where sulphoxides were obtained in acetic anhydride, attracted the present author's attention to the Pummerer reaction investigated by Horner and Kaiser[197]. It has been shown[198] that the principal pathway in the reaction of C_{10}–C_{12} dialkyl sulphoxides on heating with acetic anhydride involves the formation of α-unsaturated sulphides (a mixture of *cis*- and *trans*-isomers). The reaction is accompanied by a side process, namely the sulphone-sulphide rearrangement of the sulphoxide. The α-unsaturated sulphides obtained readily combine with diethyl phosphorodithioic acid, forming stable bifunctional derivatives of saturated sulphides—di-*O*-ethyl *S*-1-pentyl phosphorodithioates.

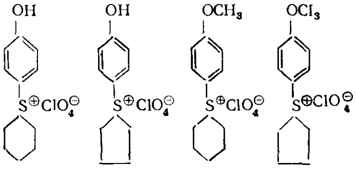
As shown above, the sulphides from the middle fractions of petroleum contain the highest concentrations of thiamonocyclanes, thiabicyclanes being next in order of abundance. When the Pummerer reaction was carried out with these sulphoxides, only the unsaturated sulphides were obtained, while the reactions with the individual substances[199] gave various results: the closest model—2-methyl-1-decalinyl sulphoxide, produced the same result—the sulphoxide was converted into the α-unsaturated 2-methyl-1-thiaoctalin; the semiaromatic 6-methyl-1-thiachromanyl sulphoxide gave 1,2-acetoxy-1-thiachromane as the main product with an admixture of the α-unsaturated 6-methyl-4*H*-benzothiapyran, which was readily converted into di-*O*-ethyl *S*-(6-methyl-1-thiachromanyl) phosphorodithioate. The reaction of thiophanyl sulphoxide with acetic anhydride gave mainly α-acetoxythiophan and, in an amount smaller by an order of magnitude, the dimer of dihydrothiophen. It has been shown[200] that thiaindan is smoothly converted into thiaindene in acetic anhydride.

Karaulova[201] showed that thiacyclanyl sulphoxides react with phenol in the presence of perchloric acid and phosphoryl chloride to form *p*-hydroxyarylthiacyclanylsulphonium salts. Sulphides can be used in this process if the condensation reaction is carried out with the same reagents in the presence of hydrogen peroxide. A Japanese study[202] served as the prototype of the first method. The present author has shown[203] that the capacity for the formation of perchlorates falls sharply in the following sequence: thiophan > thiacycloheptane > methylthiacyclohexane. 2,5-Dimethylthiophen, 2,2,6,6-tetramethylthiacyclohexane, and 2-methyl-1-thiadecalin do not form arylsulphonium perchlorates (under the conditions stated above). It has been shown that 4-hydroxyarylthiacyclanylsulphonium (aryl-4-hydroxyphenyl- or 4-hydroxynaphthyl-sulphonium) perchlorates readily undergo anion-exchange reactions, forming chlorides, phosphates, and picrates. Under the influence of potassium hydroxide in methanol, 4-hydroxyphenylthiophanylsulphonium salts yield oligomeric products, for one of which a betaine-like dimeric structure has been proposed: $(C_4H_8S.C_6H_4O)_2$.

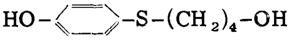
When arylthiacyclanylsulphonium salts are treated with amines[204-206], a "transonium" reaction takes place with ring opening at the C–S bond and the simultaneous addition of the base nitrogen to the ω-position of the alkyl chain: the sulphonium sulphur is converted into sulphide sulphur and amino-nitrogen forms a complex ammonium salt derived from the aminoalkyl aryl sulphide. In reactions with stronger nitrogen-containing bases, the process proceeds further; the complex ammonium salt is converted into free aminoalkyl aryl sulphide with the simultaneous formation of the ammonium salt derived from the simple amine introduced into the reaction system. This can be illustrated schematically as follows:



The reaction in the second stage involving fairly strong secondary bases proceeds quantitatively at a high rate, i.e. a simple single-stage method for the synthesis of ω-aminoalkyl aryl sulphides has in fact been found. The reactions of arylthiacyclanylsulphonium perchlorates with nucleophilic agents have been investigated in greater detail[207]. It was established that a number of arylsulphonium perchlorates

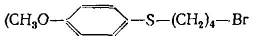


(I) (II) (III) (IV)

react with potassium iodide and picric acid to form arylsulphonium iodides and picrates. On reaction with potassium chloride, compound (I) is quantitatively converted into the chloride; compound (II) yields about 70% of the chloride and 16% of a product incorporating a heterocycle which has undergone ring opening, i.e.  (V) only on heating with an aqueous solution of potassium chloride. The metameric effect of the *p*-methoxy-group in compounds (III) and (IV) sharply reduces the extent of the exchange reaction with potassium chloride: only about 2% of the chloride of compound (III) was obtained, while that of compound (IV) was not formed. The reactions of compounds (I) and (II) with potassium bromide yield the corresponding sulphonium bromides and compound (III) gives the corresponding sulphonium bromide hydrate with an admixture of 6% of a compound of type (V). On heating with an aqueous solution of potassium bromide, compound (IV) gives rise to 12% of compound (V) and approximately 80% of compound (VI):

$$OH^- \geqslant Cl^- > Br^- > I^- \geqslant (NO_2)_2C_6H_2O^- \ .$$

Compound (VI) readily cyclises to the initial sulphonium bromide (IV); the reactions of compounds (I) and (II) with aqueous and methanol solutions of potassium hydroxide give rise to the corresponding free bases. On heating with an aqueous potassium hydroxide solution, compounds (I) and (II) form methoxyaryl derivatives of a compound of type (V), while compounds (III) and (IV) yield the corresponding methoxyaryl, methoxybutyl, or pentyl sulphides. The reactions of compounds (III) and (IV) with aqueous potassium hydroxide solutions give only complex cleavage products. The ease of dissociation of the C–S bond in the saturated heterocycle in arylthiacyclanylsulphonium salts by nucleophilic agents varies in parallel with their electronegativity§:



(VI)

The relative stabilities of the heterocycles correspond to the sequence of compounds (I) and (IV) represented above.

The compounds obtained in the reactions enumerated above are of significant interest in the study of biological activity and complex-forming properties and as starting materials for fine organic synthesis.

The involvement in these reactions of petroleum sulphides is of dual interest: (1) some of them may be suitable for the development of chemical methods for the differentiation of these sulphides into subgroups and (2) some can give rise to a mixture of substances suitable for further use without additional separation.

It is evident from all the foregoing findings that a huge advance has been made in the accumulation of data on the compositions and properties of the heteroatomic petroleum components, particularly sulphides, in the last 5–10 years. The vigorous development of research on the heteroatomic components of petroleum is only beginning. Presumably, during the coming decade, many of these components will find applications in the national economy and the elucidation of the interactions between them will open up new pathways to the rational chemical processing of petroleum and will lead to further advances in the production, transport, and utilisation of petroleum and its derivatives.

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§OH^- represents a methanolic solution of KOH.

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The Gas-phase Nitration of Alkanes

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The principal chemical and kinetic results obtained for this reaction are reported and discussed critically. A brief description is given of its industrial application to the manufacture of nitroalkanes. The detailed mechanism suggested during recent years for the nitration of alkanes by nitrogen dioxide is discussed in terms of the primary steps. The fundamental similarity of the mechanisms of nitration by nitrogen dioxide and by nitric acid is established on the basis of experimental data. A list of 119 references is included.

CONTENTS

I. LIQUID-PHASE NITRATION OF ALKANES

Towards the end of the nineteenth century Konovalov[1-3] discovered the subsequently famous method of introducing a nitro-group into an alkane or the side-chain of an alkylaromatic hydrocarbon by treatment with dilute nitric acid in sealed tubes (acid of specific gravity 1.075 at 120-130°C for 4-6 h). Since that time research on the nitration of the alkyl chain has become traditional for the Russian school of organic chemists.

During the first period, lasting until 1914, the most notable work was undertaken by Konovalov[1-10], Markovnikov[11-19], and Nametkin[20-27]. The attention paid by these eminent chemists to the nitration of saturated hydrocarbons is quite understandable. At the turn of the century the problem of the utilisation of petroleum became acute, not only as fuel but also as raw material for the production of intermediates in industrial organic synthesis. A serious obstacle to the latter use was the considerable chemical stability and hence low reactivity of saturated hydrocarbons, the main components of petroleum. Therefore any possibility of the chemical "revival" of these hydrocarbons was extremely important, and work leading to the discovery and study of chemical reactions of saturated hydrocarbons was fundamentally progressive.

During this first period the liquid-phase nitration of the alkyl chain (in alkanes, naphthenes, and alkylbenzenes) by nitric acid was closely examined by the above workers. They established experimental conditions for the reaction, the formation both of nitration products (nitro-compounds) and of oxidation products (aldehydes, ketones, alcohols, acids, and carbon monoxide and dioxide), and the qualitative and in several cases quantitative composition of the products. At the same time the first mechanisms were suggested in terms of valency-saturated intermediate and final compounds.

The first view on the mechanism of the newly discovered reaction was expressed by Konovalov in the principle that "nitric acid always nitrates initially, whatever its concentration, and oxidation is a secondary, subsequent step". Later, however, when the great stability of nitro-products to oxidation had become clear (for example, the oxidation of xylylnitromethane by nitric acid took place at temperatures 25 deg above those for the original pseudocumene), Konovalov concluded that the nitro-product underwent oxidation only at the instant of its formation.

Nametkin adopted a different approach to the mechanism of nitration. His attention was attracted by Konovalov's suggestion that, at the instant of formation by the double decomposition

$$RH + HNO_3 \rightarrow RNO_2 + H_2O$$

the nitro-compound is in an unstable state, and therefore immediately and readily undergoes further oxidation to aldehydes, ketones, alcohols, carbon monoxide and dioxide, etc. However, Nametkin regards this route to oxidation products as inconsistent with the "law of stepwise reaction "stages" formulated by Ostwald[28] as "no process leads immediately to the most stable state: the next or the least stable state of those possible is established initially". Indeed, the acceptance of such a law and of Konovalov's hypothesis leads to the conclusion that in the present case the formation of stable nitro-compounds is quite impossible, since, being in an unstable state at the instant of formation, the nitro-compound undergoes further oxidation.

An escape from the discrepancy was provided by Nametkin's hypothesis that *aci-* or iso-nitro-compounds are formed as an intermediate stage in the action of nitric acid on saturated hydrocarbons:

$$\rangle CH_2 + HONO_2 \rightarrow \rangle C{=}NOOH + H_2O$$

$$-CH_3 + HONO_2 \rightarrow -CH{=}NOOH + H_2O.$$

Under the influence of the acid medium or a high temperature these intermediates either isomerise into stable nitro-compounds or decompose by Nef's reaction into ketones (aldehydes) and nitrous oxide with subsequent oxidation of the ketone (aldehyde) to carboxylic acids.

Thus, whereas Konovalov suggested that the overall nitration involves two consecutive reactions—nitration of the hydrocarbon to the nitro-product followed by oxidation of the latter by nitric acid to oxygenated products—Nametkin postulated two parallel reactions—nitration itself and oxidation.

As we shall see later, Nametkin proved to be correct. In the light of modern views, the overall reaction of nitration actually involves two parallel chemical changes, yielding respectively nitro-products and oxygen-containing compounds. We now know that this is accomplished by means of free radicals, but the classical investigators of nitration—Konovalov, Markovnikov, and Nametkin—were unaware of this, and had to consider the mechanism of this reaction in terms of valency-saturated compounds. Nevertheless, Nametkin's hypothesis gave a fundamentally correct view of the mechanism of nitration.

On the whole all the vast and high-quality experimental information and the theoretical views developed during the first period of investigation on the reaction mechanism formed the foundation on which the subsequent intense study of the nitration of saturated hydrocarbons has continued. An astonishingly deep insight was obtained by these brilliant investigators, who were able to foresee the great value of nitration processes for the chemistry of petroleum.

II. GAS-PHASE NITRATION OF ALKANES

For two whole decades from the beginning of the First World War hardly any publications appeared on the nitration of saturated hydrocarbons: only in the mid-1930s was study of this chemical reaction resumed, not only in our own but also in other countries. However, considerable development and complication had occurred during 1914 to 1934 in the problems facing the renewed investigation, the experimental equipment in which it was now conducted, and finally theoretical views on the mechanism of complicated chemical reactions, which undoubtedly include nitration. And since the general characteristics of Konovalov nitration, the conditions under which it occurred, and (to a first approximation) its chemistry had already been established during the first period preceding 1914, research workers during the 1930s had two main tasks.

The first problem was to find optimum conditions for conducting nitration in order to secure maximum yields of the required products, which nitroalkanes had then become, having already found application. At the present time (the 1970s) the range of uses of nitroalkanes is quite wide: they are employed both as intermediates for the manufacture of nitro-alcohols, hydroxyalkylamines, and polynitro-compounds and also as solvents, stabilisers, explosives, and fuels for jet and piston engines[29].

The increasing emphasis on practical utilisation of the reaction had its natural consequence in the change in the experimental conditions under which study of the nitration of saturated hydrocarbons—mainly alkanes—was continued. Liquid-phase nitration by Konovalov's procedure, with its relatively low temperatures (120–140°C) and reaction velocities, was of no interest for industrial purposes. All researches after the mid-1930s, therefore, involved study of the nitration of the alkane chain almost exclusively in the gas phase at far higher temperatures (300–550°C). The number of nitrating agents also increased, with the use of nitrogen dioxide as well as nitric acid. This became possible after the appearance during 1934–1935 of papers by Shorygin and Topchiev[30,31], who were the first to nitrate alkanes by means of nitrogen dioxide. As will become clear from the later discussion, their discovery exerted a great influence on the whole subsequent development of research on the nitration of the alkane chain.

The second task was to elucidate the detailed mechanism of the nitration of saturated hydrocarbons. It must be stressed that the transition to the practically oriented study of nitration not only did not diminish but, on the contrary, increased interest in ascertaining the true mechanism of the process. This is quite understandable, since any extension of knowledge on the mechanism of a chemical reaction, in addition to its cognitive interest, at the same time advances the boundaries of the rational rather than the inventor's search for optimum conditions for the practical application of the reaction. But now the true mechanism of the high-temperature gas-phase reaction no longer implied merely the sequence of stable (valency-saturated) compounds. At this time the concepts of the chain theory, with its assertion of the important and decisive role of labile structures (free radicals) in the mechanism of a considerable number of high-temperature gas-phase and liquid-phase reactions, became increasingly widely accepted. Indeed, experimental information was fairly soon accumulated confirming unambiguously the participation of active centres (free radicals) in the nitration of saturated hydrocarbons. From this time elucidation of the mechanism of nitration of the alkane chain in terms of primary steps, i.e. involving free radicals, became the second task, initially sometimes not clearly understood but rather intuitively perceived by investigators.

It is clear from the above discussion that a comprehensive kinetic investigation using all the methods available for the study of this reaction was required in order to solve the second problem, the mechanism of nitration. This was by no means immediately understood—only at the end of the 1950s—some 20–25 years after resumption of investigation of the nitration of the alkane chain. This does not mean, of course, that aspects of the mechanism were completely excluded from the attention of research workers during the whole quarter-century. On the contrary, by the end of the 1930s (see below) Titov had already suggested a mechanism for the nitration of alkanes involving free radicals, which is still relevant at the present time.

The renewed investigation can conveniently be divided into two periods: the second period lasted from the 1930s to the 1960s (the first period had ended in 1914), and the third period began in the 1960s and continues at the present time. During the second period much experimental work was undertaken in establishing the industrial gas-phase nitration of alkanes, and the first investigations were made to determine the reaction mechanism in terms of primary steps, involving free radicals. The third period is characterised mainly by more detailed investigation of the reaction mechanism. The study of kinetic aspects of nitration has become considerably more intense, and the first radical-chain scheme has been suggested for nitration.

1. Development of the Industrial Production of Nitroalkanes

We shall begin our survey of results obtained during the second period with an examination of the most important work aimed at the industrial application of the nitration of alkanes. It involved essentially a search for optimum conditions for the production of nitroalkanes, and comprised two long series of studies undertaken in the U.S.A. The American papers resulted from a cooperative investigation by the Commercial Solvents Corporation and Purdue University. The first series of studies was made by Hass and his coworkers between 1934 and 1953[32-45], and the second by Bachman et al. from 1952 to 1961.[46-53]

Hass used C_1–C_6 alkanes, and was one of the first to change to high-temperature nitration in the gas phase. The experiments were made in glass or metal laboratory flow-type apparatus. The nitrating agent was either

50–70% nitric acid (at 400–700°C for up to 2 s) or nitrogen dioxide (at 250–600°C from a few seconds up to 14 min). In most cases the reaction was conducted under atmospheric pressure. Hass studied the influence of temperature, contact time, and composition of mixture (ratio of alkane to nitrating agent) on the total yields of nitroalkanes obtained in the nitration of methane [33, 38], ethane [33, 36], propane [37, 44], n-butane and isobutane [33], n-pentane [34], 2,2-dimethylbutane [41], and 2,3-dimethylbutane [40]. At the same time he determined the composition of the resulting mixture of nitroalkanes and analysed other reaction products. The possibility of increasing the yield of nitroalkanes by conducting the reaction under high pressures of methane (7 and 70 atm) [43] and ethane (7 atm),[36] as well as with additions of oxygen, nitrogen, and nitric oxide [44], was also examined.

Table 1. Nitration of alkanes by nitric acid and by nitrogen dioxide (from results obtained by Hass).

Alkane	$\frac{RH}{HNO_3}$	T, °C	Pressure, atm	Contact, s	Conversion to RNO_2,%	Nitroalkanes RNO_2					Ref.
						CH_3	C_2H_5	C_3H_7 n-	C_3H_7 iso-	C_4H_9	
Methane	9:1	475	1	0.18	13	—	—	—	—	—	38
»	12.7:1	442	1.25	2.01	16.7	—	—	—	—	—	38
»	10.5:1	444	7	0.75	27.1	—	—	—	—	—	43
»	20:1	465	70	0.28	18.8	—	—	—	—	—	43
Ethane	1—2:1	420	1	1	9	10—20	80—90	—	—	—	33
»	8—10:1	450	7	0.3	33	27	73	—	—	—	36
Propane	1—2:1	420	1	1	21	9	26	32	33	—	33
n-Butane	1—2:1	420	1	1	28	6	12	5	27	50	33
	RH:NO_2										
Propane	4:1	248	1	14 min	26	14	3	11	72	—	37
»	4:1	505—510	1	—	—	15	15	15	55	—	37
»	4:1	790—795	1	—	—	23.5	23.5	29.5	23.5	—	37

Some of the results obtained by Hass et al. are listed in Table 1. They show firstly that the rate of the gas-phase nitration of alkanes increases when nitrogen dioxide is replaced as nitrating agent by nitric acid. Hass made no attempt to explain this fact. Table 1 shows also that the ability to replace hydrogen atoms in an alkane by the nitro-group was retained on passing from the liquid-phase to the gas-phase reaction with nitric acid (and with nitrogen dioxide). Moreover, a considerable number of experimental results obtained by Hass (not included in Table 1) indicate increasing ease of substitution of a hydrogen atom in gas-phase nitration on passing from a primary to a secondary and then to a tertiary carbon atom. It is especially noteworthy that, as Hass proved, nitroalkanes are accompanied in both gas-phase and liquid-phase processes by oxygen-containing products (aldehydes, ketones, alcohols, oxides of carbon), i.e. the so called oxidising reaction path.

Naturally, there are also differences. Firstly, in contrast to the liquid-phase process, gas-phase nitration yields isomeric nitroalkanes, which means diminished selectivity of the reaction (Table 1). A second difference is the formation in the gas-phase reaction not only of nitroalkanes corresponding to the initial hydrocarbon but also lower nitroalkanes (Table 1). A third difference is the absence of polynitroalkanes in the gas-phase products, despite attempts by Hass to direct the process towards their formation; yet polynitroalkanes are almost always obtained when the reaction is conducted in the liquid phase. Fourthly and finally, alkenes are found among the products of gas-phase nitration but are absent from the liquid-phase process.

All these features are usually explained by the more severe temperature conditions of gas-phase nitration, with which we can agree. For example, the discovery by Hass that the 1-nitroalkane is formed in addition to the 2-nitroalkane on passing from the liquid phase to the gas phase is a consequence of the greater (by 4–5 kcal $mole^{-1}$) energy of a carbon–hydrogen bond attached to a primary than to a secondary carbon atom [54]: the activation energy of substitution by a nitro-group is therefore higher for a hydrogen atom at a primary than at a secondary carbon atom, so that the relative importance of the reaction leading to formation of the 1-nitroalkane should increase with rise in temperature. Furthermore, the high temperature of the gas-phase nitration of alkanes is probably the reason for the appearance of alkenes, since it is now known that the thermal decomposition of nitroalkanes leads to the formation not only of alkyl radicals and nitrogen dioxide but also of the corresponding alkene and nitrous acid [55,56].

Although Hass put forward several hypotheses [33,34,39,40,45], he was unable to relate the second difference—the formation of nitroalkanes having a smaller carbon skeleton than in the original alkane—with the higher temperature of gas-phase nitration. At the present time (the 1970s), however, it is generally accepted that alkoxy-radicals are present during the gas-phase process, and undergo thermal decomposition into aldehydes (or ketones) and alkyl radicals containing fewer carbon atoms than originally present. Reaction of these alkyl radicals with nitrogen dioxide leads to formation of the lower nitroalkanes.

Hass [44] investigated also the effect of added oxygen on the nitration of methane and propane by nitric acid dioxide at 395 and 410°C, varying the quantity of oxygen from zero to fivefold the molar proportion of the nitrating agent. With methane the conversion of nitric acid into nitromethane passed through a maximum of 24.2% when the molar ratio of oxygen was 2.6, falling to 1.4% when the ratio was 5. With propane, however, increasing the ratio of oxygen to nitrating agent from 0 to 3 produced a continuous increase in conversion of nitric acid from 28% to 62%, and of nitrogen dioxide from 13.7% to 24.7%. Unfortunately, no information was given on the effect of additions of oxygen either on decomposition of the alkane or on the composition of the nitroalkanes obtained.

On the basis of the series of investigations Hass formulated several empirical "rules" of nitration, mostly concerned with technical aspects of the process. His views on the mechanism of the nitration of alkanes, expressed in these rules, can be summarised as follows: (*a*) at moderate temperatures (300–500°C) nitration does not result in rearrangement of the carbon skeleton of the initial hydrocarbon; (*b*) under such conditions, however, oxygen-containing products and nitro-compounds undergo considerable decomposition with the formation of alkenes and degradation products (e.g. the pyrolysis of nitroethane and of 1-nitropropane yields alkanes, aldehydes, carbon monoxide and dioxide, and nitrogen, but no lower nitro-compounds); (*c*) nitration is accompanied by oxidation, with nitric acid oxidising both alkanes and nitroalkanes; and (*d*) he accepts McCleary and Degering's statement [57] (below) that nitric acid forms nitroalkanes by reaction with alkyl radicals

$$\dot{R} + HNO_3 \rightarrow RNO_2 + OH \ .$$

Bachman and his coworkers continued the studies of Hass by investigating the gas-phase nitration of propane and butane with nitric acid and nitrogen dioxide. Like Hass they examined the effects of temperature, ratio of hydrocarbon to nitrating agent, and contact time on the formation of nitroalkanes. Their results showed (Table 2) that optimum conditions for the nitration of butane comprised a ratio to nitric acid of 12.3 at 425°C for 1.6 s, when the yield of nitroalkane reached 50% of the butane consumed and 36% of the acid was converted into this product[47]. Propane could be nitrated by nitrogen dioxide most effectively at a ratio to the latter of 4.2 at 325°C with a time of contact of ~2 min, when the yield reached 51% of the propane consumed and the conversion 14–17% of the nitrogen dioxide consumed[48].

Table 2. Effects of composition of mixture, temperature, and time of contact on yield of nitroalkanes and conversion of nitrating agent into nitroalkanes (Bachman[48,49]).

Alkane	Nitrating agent	RH / Agent	T, °C	Contact	Nitroalkanes, yield, %	Nitroalkanes, conversion of HNO_3, %
C_4H_{10}	HNO_3	15	405	1.6 s	31	15
»	»	12.3	425	»	50	36
»	»	»	435	»	33	22
C_4H_{10}	HNO_3	12	425	1.6 s	38	17.4
»	»	16.2	»	»	44	24
»	»	15.6	»	»	37	15.6
C_3H_8	HNO_3	20	423	1.8 s	27.4	—
»	»	10	»	1.73 s	38.3	—
C_3H_8	NO_2	5.85	248	1.8 min	47	14
»	»	4.17	300	1.93 min	49	14
»	»	4.2	325	1.93 min	51	17

Table 3. Effect of additions of molecular oxygen on the formation of nitroalkanes RNO_2 from butane and propane (Bachman[48,49]).

Alkane	Nitrating agent	RH / Agent	NO_2 / Agent	T, °C	Contact	Yield of RNO_2, % on RH consumed	Conversion of agent into RNO_2, %	Consumption of RH, moles
C_4H_{10}	HNO_3	15	0	425	1.6 s	48	36	0.55
»	»	»	2	»	»	24	43	1.06
»	»	»	3	»	»	10	26	2.0
C_3H_8	NO_2	4–4.2	0	325	1.93 min	51	16.6	—
»	»	»	0.5	»	»	43	19.9	—
»	»	»	1.0	»	»	40	13.6	—
C_3H_8	NO_2	4–4.2	0	300	»	49	16.1	—
»	»	»	0.5	»	»	58	28.1	—
»	»	»	1.0	»	»	50	16.4	—

Having determined the maximum yields of nitroalkanes, Bachman directed his further efforts at improving the results, for which purpose he studied the effect of considerable additions of oxygen on the nitration of butane and propane[46,49]. Table 3 shows that the conversion of the nitrating agent into nitroalkanes passes through a maximum with increase in the quantity of oxygen added, whether nitric acid or nitrogen dioxide is used. He attributed this to simultaneous oxidation of the initial alkane with formation of an alkyl hydroperoxide. Breakdown of this product at the peroxy-bond to give alkoxyl and hydroxyl radicals is a branching step, which was used to explain the increasing conversion of the nitrating agent by the action of oxygen on the nitration.

Bachman's hypothesis that oxidation of the alkane takes place at the same time as its nitration is obviously correct. However, the branched character of the oxidation alone is insufficient to explain the increase in conversion, especially as later additions of oxygen beyond the conversion maximum act in the opposite direction. More detailed examination of the interaction of these two reactions is undoubtedly desirable, but several of the necessary data—primarily the consumption of the initial alkanes and frequently the composition of the resulting nitroalkanes—are lacking from the publications both of Hass and of Bachman.

Bachman studied also the effect of additions of halogens on the nitration of propane by nitric acid and by nitrogen dioxide[49,50]. The quantities of halogens were considerably smaller than those of oxygen added at the same time. Degrees of conversion and nitroalkane yields depended on the halogen concentrations. Optimum additions of chlorine and bromine were found at which maximum conversions and yields were obtained.

Bachman's experiments[47] on the influence of the ratio of the surface area of the reaction vessel to its volume S/V on the nitration of butane by nitric acid are interesting. Change in the ratio from 28 to 300 cm^{-1} at 425°C had no effect on the final results: both the degrees of conversion of butane and of nitric acid and the yield of nitroalkanes remained almost constant. Only the proportion of carbonyl compounds diminished slightly, while the quantity of carbon monoxide increased. These results most probably indicate that the reaction is homogeneous under the given conditions.

In his views on the mechanism of nitration Bachman[46] adopted all the main suggestions made by Titov (below). The only modification introduced by Bachman into Titov's set of concepts concerned the path by which nitrogen dioxide is formed during nitration by nitric acid. In 1952 Bachman was probably the first to suggest that, in the high-temperature nitration of alkanes by nitric acid, nitrogen dioxide is formed by the reaction

$$HNO_3 + M \rightarrow NO_2 + OH + M$$

which by that time had become well known and thoroughly studied.

The results obtained by Hass and by Bachman and their coworkers formed the basis for the initial trial production of nitroalkanes at Sterlington (Louisiana, U.S.A.), which was followed (in 1955) by a works manufacturing many thousands of tons a year. The process involves[58] reaction between 75% nitric acid and excess of propane under 7–9 atm (gauge) at 450°C for 1 s. Nitroalkanes and dilute acid are condensed and separated, while nitric oxide is oxidised to nitric acid and returned to the reaction vessel. Varying the conditions enables the proportions of individual nitroalkanes to be varied over the ranges 10–30% of nitromethane, 20–25% of nitroethane, and 55–65% of nitropropanes.

2. Initial Ideas on the Participation of Free Radicals in the Gas-phase Nitration of Alkanes

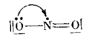
Passing now to publications during the second period of investigation that endeavoured to establish the mechanism of nitration, we shall first give the main content of the "theory of the nitration of saturated hydrocarbons and side-chains of arylalkanes", as Titov termed his investigation in his summary paper[69]. Discussing the high-temperature nitration of saturated hydrocarbons by nitrogen dioxide, he was the first to suggest[59-69] that free hydrocarbon radicals were involved, and attributed their formation to the reaction

$$RH + NO_2 \rightarrow \dot{R} + HNO_2 \,. \qquad (1)$$

However, he regarded the nitro-products as produced by the recombination of free alkyl radicals with nitrogen dioxide, which also possesses the character of a free radical:

$$\dot{R} + NO_2 \rightarrow RNO_2 \,. \qquad (2)$$

The structure of nitrogen dioxide, which can be written



to allow for interaction between the unpaired electron and the mobile *p*-electrons, enabled Titov to predict that it would react with free alkyl radicals both through the nitrogen atom and through an oxygen atom, i.e. that it would form not only nitro-compounds but also nitrites by the recombination

$$\dot{R} + ONO \rightarrow RONO \,. \qquad (3)$$

Although by the end of the 1930s Hass had shown quite reliably that nitro-compounds containing fewer carbon atoms than in the original hydrocarbon are formed in the high-temperature nitration of alkanes, his attempts to explain this fact were unsuccessful. In 1940 Titov[61] suggested a mechanism for such puzzling degradation of nitro-compounds that was based on the assumption that, under the conditions of high-temperature nitration, an alkyl nitrite undergoes pyrolysis, which according to Rice[70] should give an alkoxy-radical, whose further thermal decomposition yields an aldehyde (or a ketone) and an alkyl radical containing a smaller number of carbon atoms than in the original hydrocarbon. Thus for isobutane as example Titov wrote down the reactions

$$(CH_3)_2CH\dot{C}H_2 + NO_2 \rightarrow (CH_3)_2CHCH_2ONO \,, \qquad (3')$$

$$(CH_3)_2CHCH_2ONO \rightarrow (CH_3)_2CHCH_2\dot{O} + NO \,, \qquad (4)$$

$$(CH_3)_2CHCH_2\dot{O} \rightarrow (CH_3)_2\dot{C}H + HCHO \,, \qquad (5)$$

$$(CH_3)_2\dot{C}H + NO_2 \rightarrow (CH_3)_2CHNO_2 \,. \qquad (2')$$

The mechanism of the gas-phase nitration of alkanes by nitrogen dioxide proposed by Titov in the 1930s comprised a set of primary steps. It must be emphasised that the choice of the actual free radicals and the sequence and nature of the elementary reactions were suggested solely on the basis of results for the chemistry of nitration in terms of stable species. No kinetic study had then been made of nitration, so that information was lacking on the formal kinetics of the reaction (e.g. the effective rate constants in Arrhenius coordinates, the order of the reaction with respect to the initial substances, the kinetics with respect to pressure, etc.) and on the kinetics with respect to stable species. Thus all those data were absent, ignorance of which makes it so difficult to establish the mechanism of chemical reactions involving free radicals. The insight exhibited by Titov in formulating his mechanism is especially surprising. Indeed, as we shall see later, the chemical framework of his scheme was largely adopted by subsequent investigators.

Titov, of course, was interested in the nitration of saturated hydrocarbons not only by nitrogen dioxide but also (perhaps still more strongly) by nitric acid. He formulated the fundamental principles of this process, too. He boldly postulated that nitric acid molecules do not exert an independent nitrating action on the alkane chain but are merely the "source of the progressive regeneration" of oxides of nitrogen. Even with nitric acid, however, the true nitrating agent is still the nitrogen dioxide molecule. Nitration thus takes place, of course, by the above set of reactions (1)-(5).

In order to prove the chemical inertness of nitric acid towards the alkane chain Titov undertook special experiments on the action of the acid on various hydrocarbons[61,62,67] both in the presence of oxides of nitrogen and in their absence (achieved by the addition of urea nitrate). At temperatures up to 150°C nitric acid (specific gravity <1.4) hardly reacted with alkanes or with the side-chain of alkylbenzenes.

This result raised the question of the route by which nitric acid became the source of nitrogen dioxide. Titov suggested that nitric acid could react readily with nitrous acid and with nitric oxide, not only at high but even at low temperatures, with formation of nitrogen dioxide in both cases:

$$HNO_3 + HNO_2 \rightleftarrows 2\,NO_2 + H_2O \,, \qquad (6)$$

$$2\,HNO_3 + NO \rightleftarrows 3NO_2 + H_2O \,. \qquad (7)$$

It was emphasised that nitrous acid already appears in the first stage as a result of reaction (1), that nitric oxide is formed by secondary oxidation processes, and that both reactions (6) and (7) lead to a progressive increase in the concentration of nitrogen dioxide, even in liquid-phase nitration at low temperatures.

Somewhat later, after the publication of Hass's results showing that replacement of nitrogen dioxide by nitric acid increased the rate of the high-temperature nitration of alkanes, Titov[69] suggested that at high temperatures the formation of nitrate radicals from nitric acid was also possible:

$$\begin{array}{c} 2\,HNO_3 \rightarrow N_2O_5 + H_2O \\ N_2O_5 \rightarrow \dot{N}O_3 + NO_2 \,. \end{array} \qquad (8)$$

By analogy with the dioxide Titov represents the very rapid reaction of the above radical with the alkane chain by the equation

$$RH + \dot{N}O_3 \rightarrow \dot{R} + HNO_3 \,. \qquad (9)$$

The great activity of the nitrate radical in this reaction is attributed by Titov to purely energetic considerations and the fact that it is more strongly electrophilic than nitrogen dioxide: the former are based on the greater heat of formation of nitric than of nitrous acid; and the electrophilicity of the two species will be proportional to a first approximation to the strengths of the corresponding acids—nitric and nitrous.

Objections to certain aspects of Titov's mechanism appeared in the literature. The first was his assertion that nitrogen dioxide is formed from nitric acid by reactions (6)-(8). Bachman et al. were probably the first to reject in 1952 [46] such reaction paths in high-temperature nitration by nitric acid, and the second were Geiseler and

Reinhardt[71] in 1957. Both papers replaced reactions (6)–(8) by the thermal decomposition of nitric acid†:

$$HNO_3 + M \rightarrow OH + NO_2 + M \quad . \qquad (10)$$

This gas-phase decomposition has now been thoroughly studied[72–74], and has the rate constant

$$k = 1.6 \cdot 10^{15} \exp(-30\,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \quad .$$

Elementary calculation shows that with this rate coefficient reaction (10) is fully able to supply the quantities of nitrogen dioxide corresponding to the quantities of nitroalkanes actually obtained at 300–400°C. Indeed, the subsequent discussion will show that the Reviewers have obtained experimental evidence of the occurrence of reaction (10) as primary stage in the high-temperature nitration of the alkane chain by nitric acid.

A different situation is found with nitration by nitric acid at low temperatures (in both liquid and gaseous phases). Calculation shows that under these conditions the necessary quantities of nitrogen dioxide cannot be formed from nitric acid by reaction (10), so that a different route must be assumed. Perhaps reactions (6) to (8) occur at low temperatures, as assumed by Titov also for high temperatures. It is noteworthy that he did not study in greater detail the conditions for and the possibility of obtaining nitrogen dioxide from nitric acid at a sufficient rate at low temperatures.

The second aspect of Titov's mechanism to be refuted was the assumption that the actual nitrating agent was nitrogen dioxide even when nitric acid was used. In opposition to this several authors suggested the reaction

$$\dot{R} + HNO_3 \rightarrow RNO_2 + \dot{O}H \quad , \qquad (11)$$

which was first considered in 1938 by McCleary and Degering[57], who detected nitroethane and ethyl nitrate among the products of the action of nitric acid on tetraethyl-lead at 150°C. They suggested the scheme

$$Pb(C_2H_5)_4 \rightarrow Pb + 4\dot{C}_2H_5$$
$$\dot{C}_2H_5 + HNO_3 \rightarrow C_2H_5NO_2 + \dot{O}H$$
$$\dot{C}_2H_5 + \dot{O}H \rightarrow C_2H_5OH$$
$$C_2H_5OH + HNO_3 \rightarrow C_2H_5ONO_2 + H_2O \quad .$$

There is no doubt that the ethyl radical is present. The thermal decomposition of tetraethyl-lead has been well studied and is widely used for the production of ethyl radicals. It can thus be accepted that one of Titov's fundamental assumptions—that free alkyl radicals are involved in the formation of nitro-compounds from alkanes—found direct experimental confirmation in the above work.

However, we cannot accept that nitroalkanes are formed by reaction (11). Since at high temperatures nitric acid undergoes thermal decomposition into nitrogen dioxide and a hydroxyl radical (Eqn. 10), the competition between reactions (2) and (11) must be considered in order to choose between them. In 1967 the Reviewers[75] found experimentally that reaction (2) has zero activation energy and the rate constant $k = 2.9 \times 10^{12}$ cm^3 mole^{-1} s^{-1}. Reaction (11) takes place with incomparably greater difficulty. The few numerical data available on reactions involving abstraction by an alkyl radical not of a hydrogen atom but of a group of atoms (e.g. $\cdot CH_3 + CH_3CHO \rightarrow CH_3COCH_3 + H\cdot$ [76]) suggest that the activation energy is greater and the pre-exponential factor smaller than for abstraction of a hydrogen atom. Therefore it can reasonably be assumed that at high temperatures (300–500°C), when decomposition of nitric acid is intense, the rate of reaction (2) will be considerably higher than that of reaction (11). Indeed, if we accept that $E_{11} = 10$ kcal mole^{-1} and $A_{11} \simeq 2 \times 10^{11}$ cm^3 mole^{-1} s^{-1}, we find that at 300°C

$$\frac{W_2}{W_{11}} = \frac{k_2[R]\cdot[NO_2]}{k_{11}[R]\cdot[HNO_3]} = \frac{2.9\cdot 10^{12}[NO_2]}{2\cdot 10^{11}\cdot e^{-10000/R\cdot 573}\cdot[HNO_3]} = 0.6\cdot 10^5\,\frac{[NO_2]}{[HNO_3]} \quad .$$

Thus even if the concentration of nitrogen dioxide is only 1% of that of nitric acid, W_2 still exceeds W_{11} almost hundredfold. We therefore regard as justified Titov's assertion that nitrogen dioxide is the immediate nitrating agent in the action of nitric acid on alkanes at high temperatures.

Almost twenty years later (in 1957) Geiseler and Reinhardt[71] studied the nitration of ethane by nitric acid under atmospheric pressure at 380–460°C. They determined the effective rate constant [$k_{\text{eff}} = 4.49 \times 10^{15} \exp(-47\,500/RT)$ s^{-1}], established optimum temperatures of formation of the nitroalkanes, and studied the thermal decomposition of nitroethane. Besides obtaining important experimental data, they concluded that both Titov's reaction (2) and McCleary and Degering's reaction (11) occurred as direct acts of nitration of ethane. No evidence, either experimental or theoretical, was given that reaction (11) occurred to an appreciable extent. Therefore the Reviewers' calculation indicating the non-competitiveness of reaction (11) with (2) is still valid. This provides no support for the direct combination[71] of the mechanisms of Titov and of McCleary and Degering‡.

The assertion that nitroalkanes are formed by reaction (11) (when alkanes are nitrated by nitric acid) again appeared in the literature in 1965. Ingold and his coworkers[77] reached this conclusion from a study of the reaction between methane and nitric acid at 349.5°C, the variation in the acid concentration being followed by the infrared spectrum. These investigators discovered several interesting features: (i) the rate of decomposition of nitric acid is increased by the presence of methane; (ii) consumption of nitric acid is of the first order with respect to the acid, but only slightly dependent on methane; (iii) although nitrogen dioxide is formed during the process, it does not inhibit decomposition of the acid; and (iv) the reaction velocity is $W = 2.8k_a[HNO_3]$, where k_a is the rate constant of the decomposition of nitric acid.

In order to ascertain a mechanism of reaction between methane and nitric acid consistent with these features the authors examined the series of known elementary reactions

$$HNO_3 \xrightarrow{a} \dot{O}H + NO_2$$
$$\dot{O}H + HNO_3 \xrightarrow{b} H_2O + \dot{N}O_3$$
$$\dot{O}H + CH_4 \xrightarrow{c} H_2O + \dot{C}H_3$$
$$\dot{C}H_3 + HNO_3 \xrightarrow{d} CH_3NO_2 + \dot{O}H$$
$$\dot{C}H_3 + NO_2 \xrightarrow{e} CH_3NO_2$$
$$\dot{C}H_3 + HNO_3 \xrightarrow{f} CH_3OH + NO_2 \quad .$$

Firstly they considered non-chain mechanisms, e.g. the set of reactions *a*, *c*, and *e* or *a*, *c*, *e*, and *f*, etc., but formulae for the reaction velocity derived from these mechanisms did not satisfy the experimental data. Closest

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†Here and subsequently M represents any molecule of the reaction mixture.

‡We considered it necessary to emphasise this point, since Geiseler and Reinhardt's paper gained some publicity, and is widely quoted in the literature on the nitration of hydrocarbons.

agreement with the above experimental features was provided by the chain mechanism comprising the fundamental reactions

$$\begin{array}{l}
HNO_3 \xrightarrow{a} \dot{O}H + NO_2 \\
\dot{O}H + CH_4 \xrightarrow{c} H_2O + \dot{C}H_3 \\
\dot{C}H_3 + HNO_3 \begin{array}{l} \nearrow CH_3NO_2 + \dot{O}H \\ \searrow CH_3OH + NO_2 \end{array} .
\end{array}$$

It should be noted that Ingold et al. use CH_3NO_2 to represent the sum of nitromethane and methyl nitrite. They do not deny that reactions *b* and *f* may also occur to a slight extent. Thus the limiting stage in their mechanism is the breakdown of nitric acid into a hydroxyl radical and nitrogen dioxide. However, the main reaction yielding nitromethane and methyl nitrite is assumed to be interaction of the alkyl radical with the acid (*d*).

There can be no doubt about the first conclusion (concerning reaction *a*), at least at and above 350°C. The second conclusion—that nitromethane is formed by reaction *d*—has a quite different status. It is strange that these workers did not think of comparing, even to a first approximation, the quantitative kinetics of the two possible competing reactions *d* and *e* yielding nitromethane. The Reviewers have made such a comparison when discussing McCleary and Degering's work (above), and have concluded that the probability of the formation of nitroalkanes and alkyl nitrites by reaction *d* is very small.

It must be added that Ingold regards formation of the alcohol by reaction *f* as confirming the suggested mechanism. However, his mechanism is terminated, it may be said "compulsorily", at the stage of formation of nitromethane, and does not even involve either methyl nitrite or the alkoxy-radical (the latter is necessarily formed by the reaction $\cdot CH_3 + NO_2 \rightarrow CH_3O\cdot + NO$). Yet such an ordinary reaction as that of methoxyl with the initial alkane would undoubtedly have yielded the alcohol even without the inclusion of reaction *f* in the mechanism.

Titov's third principle—thermal decomposition into alkoxyl and nitric oxide of the alkyl nitrites formed—was refined by Gray[78]. On the basis of known thermochemical data he emphasised that the energy of the carbon–oxygen bond in an alkyl nitrite is ~57 kcal mole^{-1}, so that, when the molecule is formed by recombination of an alkyl radical with nitrogen dioxide, it possesses this energy of excitation. Gray assumes that in the liquid phase, although the energy of the adjacent oxygen–nitrogen bond is only ~37 kcal mole^{-1}, the excited alkyl nitrite can nevertheless be deactivated by collisions. The resulting stable alkyl nitrite, having lost the excess energy, must be regarded as of primary origin, formed by the single elementary reaction between the alkyl radical and nitrogen dioxide. A different situation obtains in gas-phase nitration. Here, according to Gray, the lifetime of the excited nitrite is so brief that decomposition into alkoxyl and nitric oxide takes place considerably sooner than the excess energy can be released in collisions. The analytically determinable alkyl nitrite is then formed by subsequent reaction between the alkoxy-radical and nitric oxide with formation of an oxygen–nitrogen bond, which is the weakest bond in the molecule. Such an alkyl nitrite must be regarded as of secondary origin, since its formation involves two successive elementary steps. Thus Gray's work gave rise to the problem of determining experimentally the primary or secondary origin of the alkyl nitrite (in the above senses of these terms) in the nitration of alkanes.

III. KINETICS AND MECHANISM OF THE GAS-PHASE NITRATION OF ALKANES. RADICAL-CHAIN MECHANISM OF THE NITRATION OF METHANE AND PROPANE

The above critiques[57,71,77,78] of certain aspects of the mechanism suggested by Titov completed the second period of investigation. The third period, beginning in the mid-1950s and continuing at the present time, has been characterised by steadily growing interest in the kinetics of the high-temperature nitration of the alkane chain. Such emphasis is not, of course, accidental. Only the most general idea of the mechanism of nitration had been formulated from all the preceding research. The scientific foundations of this chemical change, i.e. its detailed mechanism in terms of the quantitative kinetics of primary steps, had not been established. A more profound kinetic study of nitration therefore became necessary.

One of the first was Yoffe's study[79] of the action of nitrogen dioxide on alkanes (C_1–C_5) under static conditions at subatmospheric pressures. He discovered that nitration may take place either as a slow reaction without visible emission, as a slow reaction accompanied by light blue luminescence, or as an explosive reaction.

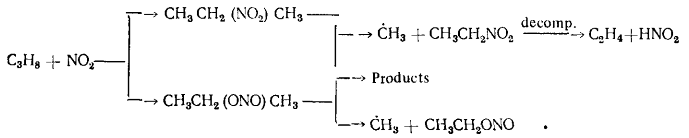
In the case of pentane the slow reaction takes place at 200–300°C. The products included primary and secondary nitroalkanes, nitric oxide, and carbon monoxide and dioxide, as well as alkyl nitrites. This worker assumed that the primary stage was detachment of a hydrogen atom from the alkane by the nitrogen dioxide. The resulting alkyl radicals react with nitrogen dioxide to yield nitroalkanes and alkyl nitrites.

With all the alkanes studied other than methane, at temperatures above 300°C and pressures above a certain limit, the reaction is accompanied by luminescence preceded by an induction period. During the latter alkyl nitrites were assumed to be formed, which decomposed into the alkoxyl and nitric oxide. The luminescence, however, may be due to reactions of the alkoxy-radical[80]. On raising the pressure (with the mixture $C_5H_{12} + 4NO_2$), Yoffe discovered a second pressure limit, above which explosion occurred accompanied by a bright white flash. This was preceded by an induction period, which could be eliminated by the addition of ethyl nitrite or shortened by acetaldehyde. With the same mixture at 400°C "composite" flames were observed, which were attributed to the dissociation $2NO_2 \rightarrow 2NO + O_2$. Analysis of the gaseous products showed in this case the presence of carbon monoxide and dioxide, nitric and nitrous oxides, and hydrogen.

Thus this work revealed several interesting features of the nitration of alkanes by nitrogen dioxide—the appearance of blue luminescence and white flames, the occurrence of an induction period, and its dependence on additions of an alkyl nitrite and of an aldehyde. The detection of an alkyl nitrite among the reaction products is significant.

Experimental results were treated differently by Myerson et al.[81], who investigated the action of nitrogen dioxide on propane at 400 and 503°C, confining their attention to the reaction accompanied by a flame. These workers observed that the colour of the flame varied from orange-red to pale blue and white depending on the pressure and the composition of the mixture. They distinguished two types of flames: (i) single-stage flames were weakly actinic; (ii) two-stage flames comprised a flame of the first type followed (after an induction period of ~9 ms) by a hot bright flame. The first flame was attributed to the formation of alkyl nitrites, but the second was regarded as due to the interaction of nitrogen dioxide with ethylene formed in the first flame. Analysis of the products showed that the first flame, when followed by the second, was accompanied by considerable reaction with the consumption of up to 20% of the propane. The main products were ethylene, methane, carbon monoxide and dioxide, nitric oxide, hydrogen cyanide, and acetylene.

The main argument used by these workers against Titov's mechanism was the absence of propene from the reaction products, which according to this mechanism they believed should have been formed in the flame by the decomposition of 2-nitropropane. The presence of a considerable quantity of ethylene instead of the expected propene and the impossibility with Titov's mechanism that it could be formed from isopropyl at subsequent stages gave these authors grounds for adopting a different mechanism of nitration, involving the formation of intermediate complexes:



Subsequent reactions of the complexes with nitrogen dioxide and (or) their decomposition yield various products, in particular nitro-compounds and alkyl nitrites having a smaller carbon skeleton than in the original alkane. Thermal decomposition of nitroethane leads to the formation of ethylene.

This mechanism with intermediate complexes is unconvincing. Immediately it was advanced Yoffe[82] made the entirely correct remark that complex formation was hardly feasible at such high temperatures (400 to 500°C). It is also hardly possible to accept the authors' statement that ethylene cannot be formed by Titov's mechanism. Actually the propoxy-radical decomposes to form the ethyl radical ($n\text{-}C_3H_7O\cdot \rightarrow C_2H_5\cdot + HCHO$), which reacts with nitrogen dioxide to give nitroethane, whose thermal decomposition yields mainly ethylene.

In spite of the doubt attaching to a mechanism involving formation of intermediate complexes, this work was important for the development of research on nitration. It continued Yoffe's study[79] of nitration accompanied by weakly actinic emission. As Myerson et al.[81] showed, such luminescence remains in the chain process, when it precedes the hot flame. We shall show below that this glow consists of slowly spreading "cool" flames, revelation of whose nature was an important turning point in establishing the kinetic mechanism of nitration.

In 1957 [sic] Gagarina and Emanuel' reported[83,84] a kinetic investigation of the reaction of methane with nitrogen dioxide under static conditions at pressures below atmospheric and at temperatures of 360–420°C. This was one of the first investigations of the gas-phase nitration of alkanes which laid stress on a kinetic study. The order of the reaction with respect to the starting materials were determined: the first order was observed with respect to methane throughout the temperature range examined; the order with respect to nitrogen dioxide varied from unity at 360 and 380 to 0.5 at 400 and 0.3 at 420°C. Determination of the order in the latter case was complicated by the fact that change in the initial pressure of nitrogen dioxide was accompanied by changes in those of nitric oxide and oxygen in conformity with the equilibrium constant (methane was introduced into the reaction vessel after the nitrogen dioxide, following establishment of the equilibrium $2NO_2 \rightleftharpoons 2NO + O_2$).

In order to ascertain whether nitric oxide and oxygen took part in the reaction, a series of experiments was made at 400°C in which the initial pressures of methane and nitrogen dioxide remained constant and only those of the test gases were varied. Increasing the concentration of nitric oxide increased the rate of reaction (measured from the increase in the total pressure), whereas addition of oxygen produced a sharp decrease. Since the effects of these gases on the reaction were not determined at all temperatures at which its order with respect to nitrogen dioxide had been determined, the authors themselves regarded their values for the order of reaction as not entirely accurate.

The effective activation energy of nitration was determined[83,84] as $E_{\text{eff}} = 42$ kcal mole^{-1}. The rate of reaction of methane with nitrogen dioxide was independent of the total pressure, and zero order was maintained during the reaction. This was attributed to the coupling of many elementary stages, involving not only intermediate species but also nitrogen dioxide and oxygen. The constant rate during the reaction is described by the empirical equation $w = k[CH_4][NO_2]/[O_2]$, where k is the effective rate constant and the square brackets indicate instantaneous concentrations of the gases.

The kinetics with respect to products showed[83,84] that the action of nitrogen dioxide on methane yields nitromethane, carbon monoxide and dioxide, nitric oxide, and small quantities of formaldehyde and hydrogen cyanide. Nitromethane was an intermediate product, but not the only one, which was confirmed by comparing its rate of consumption with the rate of increase of the total pressure at various times during the reaction. Calculation showed that around 50% of the products of intensive oxidation of methane (carbon monoxide and dioxide) is produced without intermediate formation of nitromethane.

These workers regard the step $RH + NO_2 \rightarrow R + HNO_2$ as the first stage of initiation of the reaction of alkanes with nitrogen dioxide. They consider that methane can undergo two independent reactions — nitration to nitromethane and intensive oxidation by oxygen in the nitrogen dioxide (oxidation by combined oxygen).

A study of the kinetics of the action of nitrogen dioxide on n-butane was published by Ermakova et al.[85] in 1961. Experiments were made under static conditions with subatmospheric pressures over the temperature range 250–450°C. The order of the reaction at 300°C was 0.7 and 1.4 with respect to butane and nitrogen dioxide respectively. The effective activation energy determined over the above temperature range was 30 kcal mole^{-1}. Either a slow reaction or a reaction with a hot flame was observed depending on the conditions. The temperature dependence of the explosion limit was determined for the mixture $C_5H_{10} + 6.5NO_2$ on the assumption that the explosion was thermal in nature. The primary step in the reaction was regarded as

$$n\text{-}C_4H_{10} + NO_2 \rightarrow n\text{-}\dot{C}_4H_9 + HNO_2 \text{ ,}$$

which was followed by formation either of the nitro-compound

$$\dot{C}_4H_9 + NO_2 \rightarrow C_4H_9NO_2$$

or of the alkyl nitrite

$$\dot{C}_4H_9 + NO_2 \rightarrow C_4H_9ONO \text{ .}$$

From the late 1950s to the early 1960s a comprehensive kinetic investigation of the gas-phase nitration of methane and propane was started at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences[86-100]. This was directed towards establishing the mechanism of these reactions. The latter phrase applied to a gas-phase reaction involving free radicals has a quite definite and general meaning. It includes as first stage determination of the kinetic mechanism, i.e. elucidation of whether a free-radical, unbranched-chain, ordinary branched-chain, or degenerately branched-chain reaction is involved. This entails the establishment of several kinetic laws—determination of the dependence of the reaction velocity on such factors as time, pressure, temperature, diameter of reaction vessel and the ratio of its surface to its volume, addition of inert gases and intermediate products, composition of initial mixtures, etc.

The second stage is to specify the chemistry of the kinetic mechanism, i.e. to construct a set of primary chemical steps representing in totality the true course of the chemical change. Besides the above kinetic laws great importance attaches here to determining the kinetics with respect to stable species (initial compounds, intermediates, and final products).

Finally, the concluding stage is to compare the overall reaction velocity, calculated from the proposed mechanism by a quasi-stationary method, with the observed rate. During recent years this stage has often included also a comparison of the kinetics with respect to stable reaction products, determined from the suggested mechanism by calculation on an electronic computer, with experimental results for the accumulation of products.

The nitration of methane and propane by nitrogen dioxide was studied[89,91-95,99] under static conditions in glass vacuum apparatus both at 400–600°C and 10–630 mmHg and at 200–500°C and 20–500 mmHg. The variation in the concentration of nitrogen dioxide during the reaction was recorded. The reaction products were analysed polarographically, spectroscopically, and chromatographically. Three types of reaction between alkanes and nitrogen dioxide were established (Fig. 1).[86]

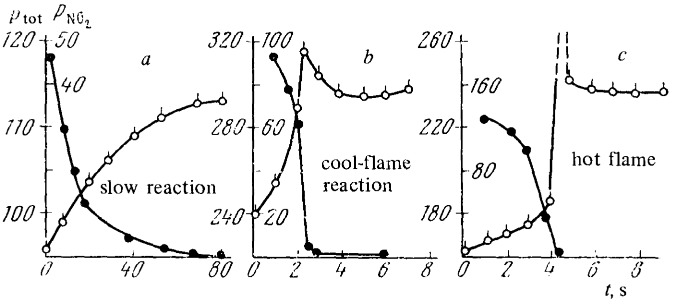


Figure 1. Kinetic curves for three types of reaction in the nitration of propane by nitrogen dioxide at 350°C: *a*) mixture of C_3H_8 + NO_2 (p_{init} = 96 mmHg); *b*) 1.5 C_3H_8 + NO_2 (237); *c*) C_3H_8 + 4NO_2 (162.5): 1) total pressure; 2) pressure of nitrogen dioxide.

1. Slow reaction. Kinetic curves based on the change in pressure Δp and the consumption of nitrogen dioxide are typical of unbranched-chain reactions. The reaction velocity is constant up to 30–50% consumption.

2. Cool-flame reaction. An autocatalytic process terminates in a jump in pressure, which is accompanied by passage through the mixture of a weakly actinic flame, termed "cool" by the authors and visible only in a darkened room. The rate of propagation of such flames is 10–20 cm s^{-1}, and the temperature in them is raised by about 100–150 deg. The nitrogen dioxide has been almost completely exhausted when the pressure peak is reached. The spectra of these cool flames indicates that their emission is due to electronically excited formaldehyde[90].

3. Reaction with a hot flame. This also begins with an autocatalytic process followed by an abrupt rise in pressure and then a rapid fall. At the instant of the jump in pressure the reaction is accompanied by a bright flame, in which it goes to completion.

Special experiments on hot flames appearing at the pressure limit and near the limit within the region of thermal ignition have confirmed that such ignition is a two-stage process[98]: the first stage involves passage of the cool flame, and is followed, in the mixture modified by the accompanying reaction, by the hot flame as the second stage. Transitions from the first to the second and then to the third type of nitration can be achieved either by increasing the pressure or by raising the temperature, and have definite limits with respect to these factors.

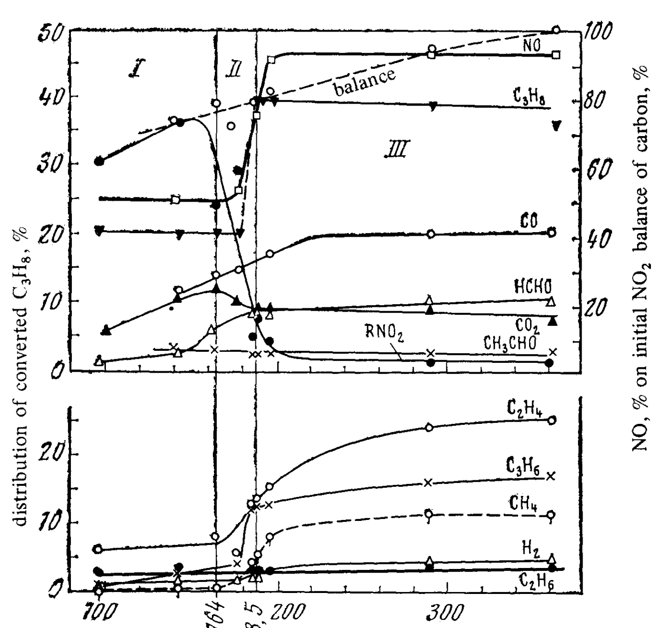


Figure 2. Composition of products at ends of slow and cool-flame reactions in the nitration of propane as function of initial pressure (C_3H_8 + NO_2 at 350°C): I) slow reaction; II) reaction "with a peak" on the pressure–time curve; III) reaction with a cool flame.

Fig. 2 shows marked differences in the composition of the products on termination of the slow and of the cool-flame reactions in the action of nitrogen dioxide on propane at 350°C. The main products of the slow reaction are nitroalkanes, carbon monoxide, and carbon dioxide, while the quantities of alkenes, carbonyl compounds, methane, and hydrogen are small. At the end of the cool-flame reaction only a minor quantity of nitroalkanes is recorded, whereas the main products are alkenes (ethylene and propene), carbon monoxide and dioxide, formaldehyde, and methane. Only carbon monoxide, carbon dioxide, and nitrogen are found at the end of the hot-flame stages[91].

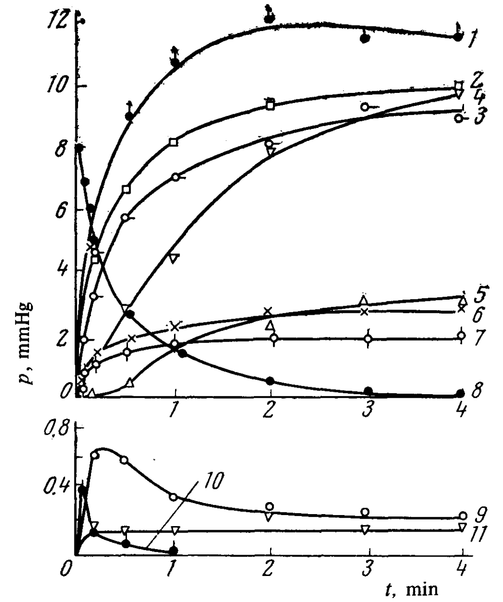


Figure 3. Rates of consumption of nitrogen dioxide and accumulation of products of the slow nitration of propane ($C_3H_8 + NO_2$ at 300°C and initially 320 mmHg): 1) $2\text{-}C_3H_7NO_2$; 2) CO_2 (×0.5); 3) CH_3NO_2; 4) CO (×0.5); 5) $(CH_3)_2CO$; 6) $1\text{-}C_3H_7NO_2$; 7) $C_2H_5NO_2$; 8) NO_2 (×0.1); 9) CH_3ONO; 10) iso-C_3H_7OH; 11) CH_3CHO.

Fig. 3 illustrates the accumulation of products throughout the slow reaction in the nitration of propane. Analysis of the products at the end of the cool-flame induction period§ gave the important result that the composition of the mixture was closely similar to that during the slow reaction. Indeed, nitroalkanes and oxides of carbon predominate at the end of this induction period, whereas methane and alkenes are almost completely absent. This suggests that the autocatalytic reaction leading to the cool flame is identical in mechanism with the slow reaction, and that the difference in composition between the products on termination of the slow and of the cool-flame reactions is due to reactions occurring in the cool flame itself as a consequence of the rise in temperature.

Determination of the order of reaction with respect to the starting materials and of the activation energy yielded formulae for the initial rates of the slow nitration of methane and propane by nitrogen dioxide[89,92]:

$$w_{CH_4+NO_2} = (7.3 \pm 0.6) \cdot 10^{14} \exp[(-33.6 \pm 0.9)/RT] \cdot [CH_4] \cdot [NO_2] \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 400—500 °C)

$$w_{C_3H_8+NO_2} = (1.0 \pm 0.1) \cdot 10^{15} \exp[(-30.0 \pm 0.5)/RT] \cdot [C_3H_8] \cdot [NO_2] \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 200—250 °C)

$$w_{C_3H_8+NO_2} = (8.5 \pm 2.5) \cdot 10^{8} \exp[(-30.0 \pm 0.5)/RT] \cdot [C_3H_8]^{0.75} \cdot [NO_2]^{1.6} \text{ mole cm}^{-3}\text{ s}^{-1}$$
(for 300—350 °C)

Studies were made[89,93] of the influence on the kinetics of nitration of varying the ratio of surface to volume *S/V* and the diameter of the reaction vessel and also of adding inert gases—nitrogen, carbon dioxide, helium—to the mixtures. Increasing the *S/V* ratio and decreasing the diameter had hardly any effect on the initial rate of the slow reaction but raised the pressure limit of cool-flame ignition. Additions of inert gases left the initial rate of the slow nitration of methane and propane almost unchanged, lowered the pressure limit for the cool-flame ignition of methane, and, rather unexpectedly, raised the pressure limit in the case of propane.

The addition of intermediate products (aldehydes and alkyl nitrites) had hardly any effect on the rate of the slow nitration of methane and propane, but shortened the induction period and lowered the pressure limit of cool-flame ignition[89,93].

The experimental results obtained made it possible to establish the kinetic mechanisms of the cool-flame and the slow nitration of methane and propane by nitrogen dioxide. With the former reaction the task was facilitated by comparison with the cool-flame oxidation of alkanes by free oxygen. Thorough investigation of this latter reaction, known for more than fifty years, indicated a chain process with degenerate branching. These two reactions were closely similar: in both cases the process began, after an induction period, with an autocatalytic reaction leading to a sharp jump in pressure accompanied by passage of a weakly actinic cool flame through the mixture; the jump was followed by a rapid drop in pressure, coinciding with extinction of the cool flame. In both cases the rate of propagation of the cool flame was 10–20 cm s^{-1}, and the temperature 100–150 deg above that of the walls of the reaction vessel. Finally, the source of the emission by the cool flame is electronically excited formaldehyde in both nitration and oxidation[90,100].

There are also differences: (*a*) only one cool flame appears in nitration, but in oxidation the number of successive cool flames may reach seven, as e.g. with propane; (*b*) all the initial reactants are consumed in the single cool flame of nitration, but only 10–20% in each of the cool flames of oxidation. However, these differences were shown[98] to be due to the negative temperature coefficient of reaction velocity characteristic of the oxidation but not of the nitration of alkanes. Therefore the differences do not disprove the similar nature of cool-flame nitration and oxidation of alkanes, and did not prevent the authors from assuming, initially by analogy, a kinetic mechanism of degenerate branching also for the cool-flame nitration of alkanes.

This conclusion is supported by several of the experimental results[89,93] for the nitration of methane and propane by nitrogen dioxide: (i) the induction period is shortened and the pressure limit of cool-flame ignition is lowered by the addition of active intermediate products (aldehydes, alkyl nitrites) to the initial mixture; (ii) increasing the *S/V* ratio and diminishing the diameter of the reaction

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§The cool-flame induction period is the time that elapses from admission of the mixture to the reaction vessel until cool-flame ignition occurs.

vessel raise the pressure limit of cool-flame ignition; and (iii) dilution of the initial mixture with nitrogen lowers the pressure limit of cool-flame ignition in the nitration of methane. The last two effects find a reasonable explanation in the termination of chains at the walls.

A degenerate-branching mechanism of cool-flame nitration appears at first glance to be inconsistent with the above rise in the pressure limit of cool-flame ignition of propane on addition of an inert gas. An explanation for the difference from methane was obtained from a consideration of paths leading to branching during nitration. Indeed, if it were possible to show that the rate of branching in the nitration of propane diminishes on addition of an inert gas, this would explain the unexpected rise of the limit. Interaction between nitrogen dioxide and aldehydes formed by the thermal breakdown of alkoxy-radicals has been regarded[95,99,100] as the branching step in nitration. It is therefore necessary to determine possible routes by which alkoxy-radicals themselves can be formed.

The first possible path is disproportionation:

$$\dot{R} + NO_2 \rightarrow R\dot{O} + NO \ .$$

Analytically determinable alkyl nitrite is then formed in a secondary stage:

$$R\dot{O} + NO \rightarrow RONO$$

i.e. is of secondary origin. A second path is formation, from the same alkyl radical and nitrogen dioxide, of excited RONO*, which is either converted by loss of excess energy in deactivating collisions into a stable nitrite of primary origin or, because of its short lifetime, breaks down into an alkoxy-radical and nitric oxide. A stable nitrite will then be formed, as in the case of disproportionation, by the reaction RO· + NO: i.e. it will be of secondary origin.

The stable methyl nitrite obtained in a study of the primary reaction between a methyl radical and nitrogen dioxide was shown[75] to be of secondary origin. Additions of an inert gas, of course, cannot influence disproportionation but may promote deactivation of an alkyl nitrite, thereby lowering the alkoxyl concentration and hence also the concentration of aldehydes, which in turn will diminish the rate of branching.

Calculations by means of Kassel's formula yield for excited methyl and propyl nitrites the relatively long lifetimes of 10^{-6} and 10^{-2} s respectively, so that they can be stabilised even at pressures below 1 atm. In this case a primary nitrite should be formed.

During recent years, however, the view has been expressed that not all bonds in a molecule are equally involved in the redistribution of energy[101,102]. In an alkyl nitrite, for example, decomposition involves rupture of the oxygen–nitrogen bond, i.e. a bond between [relatively] heavy atoms, whose vibration frequencies are considerably lower than (33–50% of) those of a carbon–hydrogen bond. Because of the absence of resonance between the frequencies of slow vibrations of the oxygen–nitrogen bond and the rapid vibrations of the carbon–hydrogen bonds, therefore, the transfer of energy to these latter bonds can be ignored. In the Kassel formula for methyl nitrite the number of effective degrees of freedom among which the energy is distributed will then decrease to 6 from 15, and hence the lifetime will be 10^{-11} s. This implies almost instantaneous breakdown into methoxyl and nitric oxide. It is impossible to stabilise such a nitrite at pressures of ~ 1 atm. Application of this method of calculation to propyl nitrite gives a lifetime of $\sim 10^{-8}$ s. Addition of an inert gas will then increase significantly the probability of deactivation, which will naturally lead to a decrease in the rate of branching, i.e. to a raising of the limit of cool-flame ignition.

Establishment of degenerate branching for cool-flame nitration was an important factor in solving the kinetic mechanism of the slow reaction. The form of the rate curves for the latter (Fig. 1*a*), the lack of effect of additions of aldehydes, alkyl nitrites, and inert gases and of variation in the S/V ratio all appeared to suggest that the slow reaction was an unbranched-chain reaction with homogeneous chain, initiation and termination. However, the Reviewers regard such a view as incorrect.

Indeed, it is impossible to reconcile a change in kinetic mechanism from degenerately branched to unbranched (which supposedly occurs on passing from cool-flame to slow nitration) with the absence[93] of any chemical differences between the slow reaction and the autocatalytic reaction leading to cool-flame ignition. The same intermediate and final products are formed in the two cases, even in the same proportions. Thus the aldehydes responsible for branching in the cool-flame reaction are formed also in the slow reaction, and it is difficult, since transition from the first to the second reaction and *vice versa* have limits with respect to both temperature and pressure, to suppose that slight variation in these parameters at the pressure limit of cool-flame ignition would be able either completely to suppress the branching power of aldehydes or to confer on them this power. It may be recalled here that the oxidation of alkanes by free oxygen also involves a limiting transition between cool-flame and slow reactions, but they are both degenerately branched processes, and the rate curves of the slow reaction (graphs of the time dependence of Δp and the aldehyde concentration) are sigmoid.

In sum the authors accept[95,99,100] that slow nitration (just like the cool-flame process) is a degenerately branched chain reaction, since steps of degenerate branching take place during its course, but one in which the rate of chain termination exceeds the rate of branching. When the rate of chain initiation is sufficient, as in nitration¶, such a reaction will mimic kinetically an unbranched-chain process.

According to the chain theory the limit equation in a degenerately branched chain reaction can be deduced from the formula

$$M=\{w_0/[k(\nu-1)-k']\}\,[e^{[k(\nu-1)-k']t}-1],$$

where the condition $k(\nu - 1) - k' = \varphi = 0$ defines the limit. Here M is the concentration of the branching agent (in the present case an aldehyde), ν the length of the chain, given by the ratio of the rates of chain propagation and chain termination, k the rate constant of degenerate branching, and k' the rate constant for termination of the branching agent. We shall see that termination of the branching agent must be introduced in order to obtain the limit. Termination of the aldehyde on the wall is assumed in the paper.

The transition from the cool-flame reaction through the limit to the slow reaction with variation in pressure (at constant temperature) can now be explained by the fact that $\varphi > 0$ in the region of cool-flame nitration. Decrease in pressure affects only k', which with termination in the diffusion domain will increase, so that φ will decrease.

¶Table 5 gives initiation rate constants for the nitration of propane. At 350°C, for example, $k_{\text{init}} = 10^{11} \times 8.5 \times 10^{-10} = 85$, which exceeds by 10^7 the value for the oxidation of propane by free oxygen.

At a certain pressure φ will become zero, and a slight further decrease in pressure will lead to transition through the limit into the region of the slow reaction.

With fall in temperature and the accompanying transition from cool-flame to slow reaction the rate constant of homogeneous termination remains unchanged, and that of surface termination decreases only slightly. A marked decrease is observed in the rate constant of branching, which, as always, has quite a high activation energy. Overall the rate of termination may exceed the rate of branching, and in contrast to ordinary branched processes, where reaction cannot in practice be measured below the limit ($\varphi < 0$), here (in nitration) a slow reaction mimicking an unbranched process is observed owing to relatively rapid initiation.

The establishment of a chain mechanism with degenerate branching for the slow and cool-flame nitration of methane and propane gave rise to the problem of the specific chemistry of this kinetic mechanism. In other words, a radical–chain scheme must be sought, unique to each hydrocarbon, calculations based on which would lead, depending on the temperature and the pressure, either to an autocatalytic cool-flame reaction ($\varphi > 0$) or to a slow reaction, involving the branching steps but mimicking an unbranched-chain process ($\varphi < 0$) because of the preponderance of termination over branching. The schemes suggested[95,99,100] for the nitration of methane and propane have the same fundamental structure, with that for methane forming part of the scheme for propane. The latter is more complicated only in involving radicals containing two and three carbon atoms in addition to those containing a single carbon atom.

Initiation is represented by the equation

$$RH + NO_2 \rightarrow \dot{R} + HNO_2 \ . \qquad (a)$$

Calculation of the activation energy of reaction (*a*) on the basis of the Polanyi–Semenov rule gave values of 30.8, 26.2, and 23.6 kcal mole^{-1} for the formation of methyl from methane and of propyl and isopropyl from propane. An important confirmation of this step (*a*) is the discovery by Soviet workers[103-107] that additions of nitrogen dioxide accelerate the oxidation of alkanes by free oxygen.

The alkyl radicals formed in reaction (*a*) undergo parallel reactions with nitrogen dioxide:

$$\dot{R} + NO_2 \rightarrow RNO_2 \qquad (b)$$

$$\dot{R} + NO_2 \rightarrow [RONO]^* \rightarrow R\dot{O} + NO \qquad (c)$$

the first of which terminates the chain, whereas step (*c*) propagates the chain. Rate constants of these steps and of $R\cdot$ + NO → RNO were determined[94,96,97] directly for the reactions of the methyl radical with nitrogen dioxide and with nitric oxide†.

The alkoxy-radicals obtained in reaction (*c*) may undergo further change in three ways—(i) unimolecular decomposition with formation of an aldehyde and a lower alkyl radical

$$R\dot{O} \rightarrow R'CHO + R'' \qquad (d)$$

and for the methoxy-radical

$$CH_3\dot{O} \rightarrow HCHO + \dot{H} \qquad (e)$$

(ii) hydrogen abstraction with formation of the alcohol

$$RO + RH \rightarrow ROH + \dot{R} \qquad (f)$$

and (iii) recombination with nitrogen dioxide and with nitric oxide, which is significant only at relatively low temperatures because of the thermal instability of alkyl nitrates and nitrites. (iv) Disproportionation of alkoxy-radicals with nitric oxide to form aldehydes (or ketones) becomes possible in the later stages, when the concentration of nitric oxide has become considerable. In the initial stages of nitration the main reaction of alkoxy-radicals is decomposition with formation of aldehydes.

The aldehydes react with nitrogen dioxide:

$$RCHO + NO_2 \rightarrow R\dot{C}O + \dot{H}NO_2 \ . \qquad (g)$$

This is a step of degenerate branching, since it entails replacement of the relatively inactive nitro-radical by an active aldehyde radical (formyl in the nitration of methane, and acetyl in that of propane). Published experimental rate constants k_{eff} for the reactions of acetaldehyde and of formaldehyde with nitrogen dioxide are closely similar to the rate constants of the primary steps (*g*). Although the assumed branching is of degenerate type, its rate constant is closer to the value for branching in the oxidation of molecular hydrogen than to the rate constant of degenerate branching in the oxidation of alkanes.

The resulting acetyl radical reacts mainly with nitrogen dioxide according to the equation

$$CH_3\dot{C}O + NO_2 \rightarrow \dot{C}H_3 + CO_2 + NO \ .$$

Competing processes—decomposition of the acetyl radical and its reaction with nitric oxide—are considerably slower under the given conditions, and therefore were omitted from the scheme. Examination of published information on the reaction of formaldehyde with nitrogen dioxide led to the inclusion of three reactions of the formyl radical—chain termination

$$H\dot{C}O + NO_2 \rightarrow CO + HNO_2 \qquad (i)$$

and chain propagation

$$H\dot{C}O + NO_2 \rightarrow CO_2 + \dot{H} + NO \qquad (j)$$

$$H\dot{C}O + M \rightarrow \dot{H} + CO + M \ . \qquad (k)$$

The hydrogen atoms formed in reactions (*e*), (*j*), and (*k*) undergo with nitrogen dioxide the rapid chain-propagating reaction

$$\dot{H} + NO_2 \rightarrow \dot{O}H + NO \qquad (l)$$

which takes place at almost every collision. The resulting hydroxyl radical reacts with the alkane:

$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \ . \qquad (m)$$

The step $HO\cdot + NO_2 \rightarrow HNO_3$ is a third-order reaction which is considerably slower than (*m*). The nitrous acid formed in several stages breaks down almost immediately: $2HNO_2 \rightarrow H_2O + NO_2 + NO$. Heterogeneous termination of aldehydes has been introduced into the scheme.

Calculations based on the schemes for the reactions of propane and methane with nitrogen dioxide were made by the method of quasi-stationary states, on the hypothesis that, since aldehydes react relatively rapidly with nitrogen dioxide, they are the active centres of the reaction. Among all active centres only aldehydes (acetaldehyde and formaldehyde) show a non-zero variation of concentration with time, since they are involved in the slow stage of degenerate branching. Calculation on the

†The reaction $R\cdot$ + NO → RNO, whose rate constant was considerably smaller than that of the reaction $R\cdot + NO_2$, is ignored in the scheme for the initial stages of reaction, when the concentration of nitric oxide is still small.

scheme for the nitration of propane was based on the assumptions that

$$k_1 = k_4 = k_7 = k_{17} = 0.45\,k_2\ ;\ \ k_2 = k_5 = k_8 = k_{18}; \qquad (1)$$

$$[\text{n-}C_3H_7] : [\text{iso-}C_3H_7] = 0.25\ . \qquad (2)$$

	Scheme of nitration of propane	Q, kcal mole^{-1}
0.	$C_3H_8 + NO_2 \xrightarrow{k_0} \text{n-}\dot{C}_3H_7 + HNO_2$	—19.6
	$C_3H_8 + NO_2 \xrightarrow{k_{01}} \text{iso-}\dot{C}_3H_7 + HNO_2$	—16.2
1.	$\text{n-}\dot{C}_3H_7 + NO_2 \rightarrow CH_2(NO_2)CH_2CH_3$	+ 59.6
2.	$\text{n-}\dot{C}_3H_7 + NO_2 \rightarrow \text{n-}C_3H_7ONO \rightarrow \text{n-}C_3H_7\dot{O} + NO$	+ 18.5
3.	$\text{n-}C_3H_7\dot{O} \rightarrow \dot{C}_2H_5 + HCHO$	—11.3
4.	$\dot{C}_2H_5 + NO_2 \rightarrow C_2H_5NO_2$	+ 55.6
5.	$\dot{C}_2H_5 + NO_2 \rightarrow [C_2H_5ONO^*] \rightarrow C_2H_5\dot{O} + NO$	+ 14.3
6.	$C_2H_5\dot{O} \rightarrow \dot{C}H_3 + HCHO$	—10.3
7.	$\dot{C}H_3 + NO_2 \rightarrow CH_3NO_2$	+59.7
8.	$\dot{C}H_3 + NO_2 \rightarrow [CH_3ONO^*] \rightarrow CH_3\dot{O} + NO$	+15.8
9.	$CH_3\dot{O} + NO \rightleftarrows CH_3ONO$	+ 40.7
10.	$CH_3\dot{O} \rightarrow \dot{H} + HCHO$	— 20.9
11	$HCHO + NO_2 \rightarrow H\dot{C}O + HNO_2$	—8.7
12.	$H\dot{C}O + NO_2 \rightarrow CO + HNO_2$	+59.8
13.	$H\dot{C}O + NO_2 \rightarrow \dot{H} + CO_2 + NO$	+ 33.5
14.	$H\dot{C}O + M \rightarrow \dot{H} + CO + M$	— 18.4
15.	$\dot{H} + NO_2 \rightarrow \dot{O}H + NO$	+ 29.0
16.	$\dot{O}H + C_3H_8 \rightarrow \text{n-}\dot{C}_3H_7 + H_2O$	+ 20.2
	$\dot{O}H + C_3H_8 \rightarrow \text{iso-}\dot{C}_3H_7 + H_2O$	+ 25.2
17.	$\text{iso-}\dot{C}_3H_7 + NO_2 \rightarrow CH_3CH(NO_2)CH_3$	+ 58.8
18.	$\text{iso-}\dot{C}_3H_7 + NO_2 \rightarrow [\text{iso-}C_3H_7ONO^*] \rightarrow \text{iso-}C_3H_7\dot{O} + NO$	+ 16.5
19.	$\text{iso-}C_3H_7\dot{O} \rightarrow CH_3CHO + \dot{C}H_3$	—6.9
20.	$\text{iso-}C_3H_7\dot{O} + C_3H_8 \rightarrow \text{n-}\dot{C}_3H_7 + \text{iso-}C_3H_7OH$	+ 4
	$\text{iso-}C_3H_7\dot{O} + C_3H_8 \rightarrow \text{iso-}\dot{C}_3H_7 + \text{iso-}C_3H_7OH$	+ 8
21.	$CH_3CHO + NO_2 \rightarrow CH_3\dot{C}O + HNO_2$	— 8.9
22.	$CH_3\dot{C}O + NO_2 \rightarrow \dot{C}H_3 + CO_2 + NO$	+ 35.9
23.	$CH_3CHO \xrightarrow{\text{walls}} \text{termination}$	—
24.	$HCHO \xrightarrow{\text{walls}} \text{termination}$	—
25.	$2\,HNO_2 \rightarrow NO_2 + NO + H_2O$	—

	Scheme of nitration of methane	Q, kcal mole^{-1}
0′.	$CH_4 + NO_2 \rightarrow \dot{C}H_3 + HNO_2$	—25.7
1′.	$\dot{C}H_3 + NO_2 \rightarrow CH_3NO_2$	+ 59.7
2′.	$\dot{C}H_3 + NO_2 \rightarrow [CH_3ONO^*] - CH_3\dot{O} + NO$	+ 15.8
3′.	$CH_3\dot{O} + CH_4 \rightarrow \dot{C}H_3 + CH_3OH$	— 0.6
4′.	$CH_3\dot{O} \rightarrow HCHO + \dot{H}$	—20.9
5′.	$HCHO + NO_2 \rightarrow H\dot{C}O + HNO_2$	—8.7
6′.	$H\dot{C}O + M \rightarrow \dot{H} + CO + M$	— 18.4
7′.	$H\dot{C}O + NO_2 \rightarrow CO + HNO_2$	+ 59.8
8′.	$H\dot{C}O + NO_2 \rightarrow \dot{H} + CO_2 + NO$	+ 33.5
9′.	$\dot{H} + NO_2 \rightarrow \dot{O}H + NO$	+ 29.0
10′.	$\dot{O}H + CH_4 \rightarrow \dot{C}H_3 + H_2O$	+ 15.3
11′.	$HCHO \xrightarrow{\text{walls}} \text{termination}$	—
12′.	$2HNO_2 \rightarrow NO_2 + NO + H_2O$	—

Differential equations were obtained for the time dependence of the concentration of aldehydes, whose integration (with the condition that the aldehyde concentration is zero at $t = 0$) yielded for the nitration of propane the formula

$$[HCHO] = \frac{C}{A} \cdot \frac{k_0\,[C_3H_8] \cdot [NO_2]}{1+n} \cdot \frac{1}{\varphi} \cdot (e^{\varphi t} - 1)\ ,$$

where

$$\varphi = f - g = \frac{[NO_2]}{1+n}\left\{\left[k_{11}\,\frac{C}{A} + nk_{21}\left(\frac{C}{A} + B\right)\right] - \left(k_{11} + nk_{21}\left[1 + \frac{C}{1{,}4\,A}\left(0.4 + \frac{k_9\,[NO]}{k_9\,[NO] + k_{10}}\right)\right] + \frac{C}{A} \cdot \frac{k_{11}k_{12}\,[NO_2]}{(k_{12} + k_{13})\,[NO_2] + k_{14}\,[C_3H_8 + NO_2]}\right)\right\} - \frac{k_{24} + nk_{23}}{1+n}$$

in which

$$A = k_{19}\left(0.9 + \frac{0.83\,k_9\,[NO]}{k_9\,[NO] + k_1}\right) + k_{20}\,[C_3H_8]\left(0.62 + \frac{0.13\,k_9\,[NO]}{k_9\,[NO] + k_{10}}\right);$$

$$B = \frac{0.7\,k_{10}}{k_9\,[NO] + k_{10}}\ ;$$

$$C = (1 + B)\,k_{19} + 0.25\,(k_{19} + k_{20}\,[C_3H_8])\left[1 + \frac{k_5}{k_4 + k_5}(1 + B)\right];$$

$$n = [CH_3CHO]/[CH_2O],$$

and f and g are the rate constants of chain branching and termination respectively. An analogous calculation for the nitration of methane gave

$$[HCHO] = \frac{k_{2'}k_{4'}}{k_{1'}k_{3'}\,[CH_4] + k_{4'}} \cdot k_{0'}\,[CH_4]\,[NO_2] \cdot \frac{1}{\varphi}\,(e^{\varphi t} - 1)\ ,$$

where

$$\varphi = k_{5'}\,[NO_2]\left[\frac{k_{2'}k_{4'}\,\{k_{6'}\,[CH_4 + NO_2] + k_{8'}\,[NO_2]\}}{k_{1'}\,\{k_{3'}\,[CH_4] + k_{4'}\}\,\{k_{6'}\,[CH_4 + NO_2] + k_{7'}k_{8'}\,[NO_2]\}} - 1\right] - k_{11'}\ .$$

The condition $\varphi = 0$ implies a transition from a slow steady-state reaction to the non-stationary cool-flame reaction. Calculation of φ by means of equations based on the schemes showed that with rise in temperature and increase in pressure φ passes from negative to positive values, i.e. that the slow reaction passes into the cool-flame reaction. This transition agrees satisfactorily with experiment (the bottom line in Table 4 gives the observed limits of cool-flame ignition).

Table 4. Variation of φ (s^{-1}) with temperature and pressure (for the mixtures C_3H_8 + NO_2 and $4CH_4$ + NO_2).

p_{init}, mmHg	C_3H_8+NO_2			$4CH_4$+NO_2
	300° C	350° C	400° C	450° C
50	—	—	—2.4	—
100	—1.6	—1.2	—0.04	—1.9
200	—0.7	+0.15	+2.3	+0.04
400	+0.02	+0.70	—	+1.5
500	—	—	—	+1.9
Expt. p_{lim}, mmHg	360	164	70	160

Values of φ were calculated from the rate constants listed in Table 5. Rate constants for the loss of aldehydes on the walls of the reaction vessel were calculated for termination of the aldehydes by reactions *23*, *24*, and *11′* in the diffusion range: $k_{\text{loss}} = 8D/r^2$, in which the diffusion coefficient was found by means of the formula $D = \frac{1}{3}u\lambda$, where u is the velocity of the molecules, λ the free path, and r the radius of the reaction vessel. The rate constants of the loss of formaldehyde and acetaldehyde at the walls are $k_{24} = 1.0$ s^{-1} and $k_{23} = 0.7$ s^{-1} for the nitration of propane under an initial pressure of 200 mmHg at 350°C, and $k_{11'} = 1.3$ s^{-1} for the nitration of methane under the same initial pressure at 450°C.

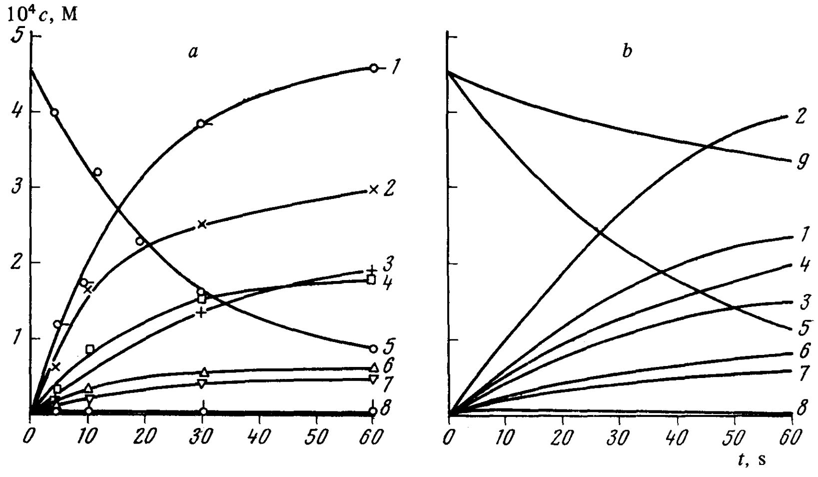

Figure 4. Comparison of (*a*) experimental and (*b*) computed curves for the accumulation of reaction products and the consumption of starting materials (C_3H_8 + NO_2 initially at 320 mmHg and 300°C): 1) CO_2; 2) 2-$C_3H_7NO_2$; 3) CO; 4) CH_3NO_2; 5) NO_2 (×0.1); 6) 1-$C_3H_7NO_2$; 7) $C_2H_5NO_2$; 8) CH_3CHO; 9) C_3H_8.

Table 5. Rate constants of primary steps.

Numbered reactions in schemes		lg *A*	*E*, kcal mole^{-1}	Experimental or estimated, Ref.
C_3H_8	CH_4			
0		11 (cm^3 mole^{-1} s^{-1})	26	est. [108]
01		11 »	24	est.
1, 4, 7, 17	1′	12.1 »	0	expt. [75]
2, 5, 8, 18	2′	12.3 »	0	expt.
3		9.6 (s^{-1})	13	est. [108, 95]
6		9.6 »	13	expt. [109]
9		10.5 (cm^3 mole^{-1} s^{-1})	0	calc. [110]
10	4′	13 (s^{-1})	24	est. [108]
11	5′	12 (cm^3 mole^{-1} s^{-1})	19	expt. [111]
12	7′	11.48 »	0	est. [108]
13	8′	11.88 »	0	est.
14	6′	14.5 »	12	est.
15	9′	13.63 »	0	expt. [112]
16		12.86 »	1.3	expt. [113]
19		11.8 (s^{-1})	17.3	expt. [114]
20		12.8 (cm^3 mole^{-1} s^{-1})	9.0	est. [108]
21		11.28 »	15.2	expt. [115]
22		12 »	0	expt. [116]
23		0.5* s^{-1}	—	est. [95]
24		0.9* s^{-1}	—	est. [95]
	3′	11.8 (cm^3 mole^{-1} s^{-1})	11	est. [117]
25		11.8** »	—	est. [108]

*Rate constant at 300°C and 320 mmHg.
**Rate constant at 300°C.

The mechanism suggested for the nitration of propane was tested also by numerical integration on an electronic computer of the set of differential equations describing the mechanism[108]. In view of the peculiarity of schemes comprising reactions of stable species and free radicals having rate constants differing by many orders of magnitude, use was made of a special algorithm and a programme developed in the Moscow State Pedagogic Institute[118,119]. The algorithm was based on solution of the set of differential equations by a finite-difference method with a "reverse step" procedure. Rate curves were computed for the consumption of the starting materials and the accumulation of the final products from an initial equimolecular mixture of propane and nitrogen dioxide under 320 mmHg at 300°C. The rate constants used for the calculation are given in Table 5‡. The computed curves are shown in Fig. 4*b*, and the corresponding experimental results are plotted in Fig. 4*a*. Since the reaction scheme has been set up for the initial stages and disregards secondary reactions of stable species (e.g. further reactions of the nitroalkanes), the suggested mechanism must be regarded as describing satisfactorily the nitration of propane by nitrogen dioxide.

The situation is less satisfactory with respect to the mechanism of the nitration of alkanes by nitric acid. As has been shown above, no agreement is apparent in the literature even on the nature of the direct nitrating agent, whether nitric acid itself or nitrogen dioxide formed by its decomposition. This question must be settled first of all, since if the role of nitric acid were mainly to generate nitrogen dioxide, the whole of the above mechanism should form the major part of the mechanism of nitration by nitric acid. This does not mean, of course, that changing from nitrogen dioxide to nitric acid does not introduce any changes into the reaction mechanism. In particular, the formation of hydroxyl radicals (by the decomposition of nitric acid) would increase the rate of nitration. Nor is heterogeneous decomposition of the acid excluded, which would affect the whole course of the reaction. Overall, however, the mechanism of nitration by nitric acid, with R + NO_2 → RNO_2 as the principal step, will be closely similar to the suggested mechanism of nitration by nitrogen dioxide.

These considerations led the Reviewers to undertake, at the Institute of Petrochemical Synthesis during recent years, experimental studies of the nitration of propane by nitric acid with the primary aim of ascertaining whether nitrogen dioxide is involved in formation of the nitrocompound[108]. Several facts have now been established: (i) the reaction of propane with nitric acid follows (as with nitrogen dioxide) three kinetic types—slow, cool-flame, and with a hot flame—depending on the temperature and

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‡For computer purposes reactions *23*, *24*, and *11′* were written $CH_3CHO \rightarrow CH_4 + CO$ *23* and $HCHO \rightarrow H_2 + CO$ *24*.

the pressure; (ii) the products at the ends of slow and cool-flame reactions are closely similar in composition to the corresponding products obtained with nitrogen dioxide; (iii) in the slow reaction autocatalysis is observed both in the accumulation of nitrogen dioxide and of nitroalkane and in the increase in pressure Δp; (iv) the time variation of the concentration of nitrogen dioxide passes through a maximum; and (v) the ratio of the rates of accumulation of nitroalkanes to the rate of accumulation of nitrogen dioxide approaches zero at shorter times. These five points can be supplemented by (vi) the Reviewers' calculation (Section II, 2) of the rates of $R^{\cdot} + HNO_3 \rightarrow RNO_2 + OH^{\cdot}$ and $R^{\cdot} + NO_2 \rightarrow RNO_2$, which indicated that at 350°C the rate of the latter exceeded that of the former reaction by $\sim 10^5$. Points (i) and (ii) are evidence of the far reaching similarity in phenomenology and closely related chemistry of the actions of nitric acid and of nitrogen dioxide on propane. Point (iv) confirms that nitrogen dioxide is actually present during the reaction with nitric acid. Point (v) implies that nitroalkanes and nitrogen dioxide are formed in two consecutive reactions, with the latter formed first, i.e. that nitrogen dioxide is involved in the formation of nitroalkanes.

Together with point (vi) all this leads to adoption of $R^{\cdot} + NO_2 \rightarrow RNO_2$ as immediate step in nitralkane formation even when nitric acid is used. As noted above, the consequence of this should be a fundamental similarity in the mechanisms of nitration of alkanes by nitrogen dioxide and by nitric acid. Only slight differences can be expected, one of which is indicated by point (iii). The continuing study of the nitration of alkanes by nitric acid being conducted at the Institute of Petrochemical Synthesis has the aim of revealing also the detailed mechanism of this reaction.

The above outline reflects the evolution of views and modern ideas on the mechanism of the gas-phase nitration of alkanes, a field in which the main contribution was made by Konovalov, Markovnikov, Nametkin, Titov, ad and Topchiev. The present issue is dedicated to the memory of S. S. Nametkin, who was the first to help elucidate the mechanism of nitration by the fruitful application of contemporaneous physicochemical concepts—e.g. the influence of the relative concentrations of the initial reactants on yields of nitration and oxidation products, the dependence of the yields of nitro-products on reaction velocity and of the latter on the "mass" of the acid, and the concept of oxidation and nitration as parallel reactions—which made nitration a subject of investigation also in physical chemistry, in particular chemical kinetics. The study of nitration in relation to neighbouring branches of chemistry has been responsible for the considerable progress made in establishing its mechanism that we now witness.

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Hydro-dehydropolymerisation and Isomerisation Polymerisation of Unsaturated Hydrocarbons

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Consideration is given to the effect of hydro-dehydropolymerisation, discovered by S.S.Nametkin and his coworkers in a study of the polymerisation of unsaturated hydrocarbons under the influence of sulphuric acid and aluminium chloride. This phenomenon is significant in the investigation of the oligomerisation and polymerisation of alkenes in the presence of various catalysts. Research on the monomer-isomerisation polymerisation of alkenes is analysed. A list of 53 references is included.

CONTENTS

I. INTRODUCTION

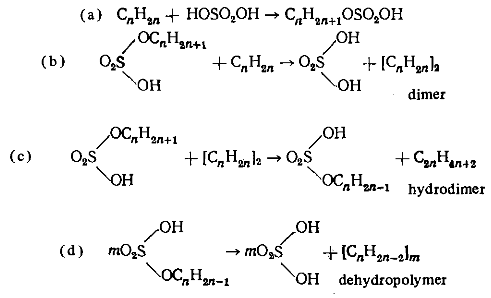
The formation of polymers by the action of sulphuric acid, aluminium chloride, and other acidic reagents on unsaturated hydrocarbons long ago attracted the attention of chemists, from Butlerov to the present time. After only a century many hundreds of papers on aspects of the polymerisation of unsaturated hydrocarbons are published annually in various chemical periodicals. Butlerov himself showed[1] that unsaturated hydrocarbons undergo polymerisation in the presence of sulphuric acid, with the formation of unsaturated compounds of higher molecular weight. The polymerisation of different types of unsaturated hydrocarbons and their derivatives has since been the subject of numerous investigations of various kinds. However, many aspects of the catalytic polymerisation of alkenes, in particular cationic polymerisation, have remained obscure.

Here we cannot consider the whole multiplicity of processes in the polymerisation of alkenes under the influence of acidic catalysts. These problems have been covered in a monograph and many review papers[2-4].

The present issure of Uspekhi Khimii is dedicated to the memory of S.S.Nametkin, whose researches on the reactions of unsaturated hydrocarbons in the presence of sulphuric acid and aluminium chloride led to the discovery of a new reaction, which he termed hydro-dehydropolymerisation. In addition, special attention is paid to monomer-isomerisation polymerisation, as an example of the variety of reactions involved in the polymerisation of alkenes. Nametkin's work on polymerisation resulted also from a non-trivial approach to the peculiarities of a well known chemical reaction.

II. HYDRO-DEHYDROPOLYMERISATION OF ALKENES WITH SULPHURIC ACID AND ALUMINIUM CHLORIDE

In his investigation of the reactions of unsaturated hydrocarbons in the presence of sulphuric acid Nametkin observed[2] the somewhat anomalous simultaneous formation of polymerisation products containing both unsaturated and saturated hydrocarbons[5]. He concluded that this was the result of the concerted occurrence of polymerisation, hydrogenation, and dehydrogenation. Polymers of saturated character, hydropolymers, were formed. The acid polymerisation of unsaturated hydrocarbons can in this case be represented by the general scheme[5]



$$\begin{aligned}
&(a)\quad C_nH_{2n} + HOSO_2OH \rightarrow C_nH_{2n+1}OSO_2OH\\
&(b)\quad O_2S\begin{matrix}OC_nH_{2n+1}\\OH\end{matrix} + C_nH_{2n} \rightarrow O_2S\begin{matrix}OH\\OH\end{matrix} + \underset{\text{dimer}}{[C_nH_{2n}]_2}\\
&(c)\quad O_2S\begin{matrix}OC_nH_{2n+1}\\OH\end{matrix} + [C_nH_{2n}]_2 \rightarrow O_2S\begin{matrix}OH\\OC_nH_{2n-1}\end{matrix} + \underset{\text{hydrodimer}}{C_{2n}H_{4n+2}}\\
&(d)\quad mO_2S\begin{matrix}OH\\OC_nH_{2n-1}\end{matrix} \rightarrow mO_2S\begin{matrix}OH\\OH\end{matrix} + \underset{\text{dehydropolymer}}{[C_nH_{2n-2}]_m}
\end{aligned}$$

which was proved correct by examining the composition of intermediate and final products.

A later study in Nametkin's laboratory of certain aspects of the preparation of isopropyl alcohol showed that hydro-dehydropolymerisation takes place in the course of the hydration of propene to propan-2-ol by means of sulphuric acid[6]. Other catalysts also effect hydro-dehydropolymerisation. Nametkin et al.[7] made a detailed study of this process when aluminium chloride acts on unsaturated hydrocarbons, in particular ethylene, pentene, etc. They pointed out that the action of aluminium chloride is complicated by partial degradation of the hydrocarbons. Subsequently Nametkin and his coworkers showed that hydro-dehydropolymerisation is observed with a wide range of unsaturated hydrocarbons of various classes. It was thus demonstrated experimentally[8] that the action of aluminium chloride on cyclohexene yields products whose formation can be explained in terms of this phenomenon. They included[8] two hydrocarbons—an unsaturated pentamer of cyclohexene (tetracyclohexylcyclohexene) and tetracyclohexylbenzene—of relatively high molecular weight. Reporting this extremely curious experimental fact, Nametkin pointed out that "the immediate mechanism of the formation of the aromatic derivative and equally of the accompanying naphthenes is still not clear, and further research is required to elucidate the routes by which they are formed". The hydropolymerisation of unsaturated hydrocarbons was later studied by Nametkin on 3-methylbut-1-ene treated with sulphuric acid monohydrate[9].

The above results suggest that the new phenomena, discovered by Nametkin and his coworkers in the polymerisation of unsaturated hydrocarbons under the influence of sulphuric acid or aluminium chloride, are general in character. They were of substantial value for the understanding of several complicated reactions involved in the production from unsaturated hydrocarbons of several technically important products (in particular, components of certain lubricating oils).

It must be borne in mind that, when aluminium chloride is used as catalyst, polymerisation is nearly always complicated by degradative effects, leading to the formation among the reaction products of compounds in which the number of carbon atoms is not a multiple of the number in the initial alkene.

A later paper by coworkers of Nametkin showed[10] that cyclopentene undergoes interesting reactions under the influence of aluminium chloride, and established for the first time the formation from cyclopentene of spirodecane. They suggested that the monomer initially dimerises, after which one ring of the dimer expands to a six-membered ring (by incorporating a carbon atom of the second ring). Trimers, tetramers, and hexamers would be formed in the same way. Unfortunately, direct evidence of the hypothetical mechanism could not be supplied at that time. In a systematic survey of several experimental investigations Rudenko[11] stated that the formation of hydropolymers from several alkenes in the presence of aluminium chloride results from a redistribution of hydrogen between the hydrocarbons forming a complex with the catalyst and the polymers. The hydrogen donors are catalytic complexes, which is confirmed experimentally by their highly unsaturated state.

In the above papers Nametkin, having examined critically results published by that time on the polymerisation of unsaturated hydrocarbons, points out that the proposed division of polymerisation processes into thermal and catalytic is incorrect. He considers that the only correct criterion for a classification of the polymerisation reactions undergone by unsaturated hydrocarbons is the composition of the products. He therefore proposes the following classification[5].

1. Polymerisation. The formation from unsaturated hydrocarbons of likewise unsaturated dimers, trimers, etc. had first been observed by Butlerov. Polymerisation may take place either at low temperatures under the influence of various catalysts (dilute sulphuric acid, zinc chloride, etc.) at high pressures and temperatures (thermally or catalytically, in particular in the presence of phosphoric acid).

2. Hydro- and dehydro-polymerisation. This process differs from polymerisation in yielding saturated hydropolymers and simultaneously highly dehydrogenated products from the unsaturated hydrocarbons. Since these products are formed at the same time, the total quantity of hydrogen involved in the reactions can be balanced.

Alkenes of iso-structure exhibit less tendency to hydropolymerisation than do the straight-chain hydrocarbons. Nevertheless, effects due to hydro-dehydropolymerisation must sometimes be reckoned with in such technically important processes as the polymerisation of isobutene. Special additives for synthetic oils are among the important products obtained from isobutene. One of the very first studies in this field, made[12] under Nametkin's direction, established that the polymerisation of isobutene in the presence of aluminium chloride (3%) at low temperatures (−78°C) yields a rubberlike polymer of molecular mass 20 000–30 000, which the authors named "superol". Several methods for obtaining polyisobutene have now found practical application, but their discussion lies outside the scope of the present Review.

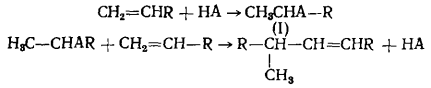
Hydro-dehydropolymerisation has since been observed on other catalysts. One of the first monographs on the catalytic polymerisation of alkenes in motor fuel[13] mentions that, in the presence of phosphoric acid at sufficiently high temperatures (up to 300°C), polymerisation is accompanied by hydro-dehydropolymerisation, so that the unsaturated compounds obtained are accompanied by saturated—including cyclic—hydrocarbons.

III. REDISTRIBUTION OF HYDROGEN IN THE REACTIONS OF UNSATURATED HYDROCARBONS ON ALUMINOSILICATE AND OTHER CATALYSTS

During the 1940–1950s the attention of investigators was especially attracted to the reactions of hydrocarbons on aluminosilicate catalysts, which acquired exceptionally important industrial value in the cracking of petroleum products. Such catalysts served and continue to serve as subjects of thousands of publications, which, of course, we do not intend even partly to survey here. The attention of the reader will be directed merely to several studies which definitely established common features in the mechanism of the action of acidic and aluminosilicate catalysts and revealed the occurence of the hydro-dehydropolymerisation of hydrocarbons on the latter.

An example is the investigation of Petrov and Frost[14], planned in some measure as a continuation of the classical studies of Lebedev and his coworkers[15], who were the first to report the redistribution of hydrogen in the transformation of unsaturated hydrocarbons on Floridin (the investigation was made on di-isobutylene and di-isopentylene [*sic*]). Petrov and Frost aimed to study the influence of the structure of the initial hydrocarbon on hydrogen redistribution on an aluminosilicate. They found that the yield of saturated products formed by hydro-dehydropolymerisation in a series of linear alkenes increases with the length of the hydrocarbon chain. This rule does not apply to cycloalkenes.

Aluminium silicate can be formulated $(HAlSiO_4)_n$ or in abbreviated form HA (i.e. it is analogous to an inorganic acid), and is able to exchange its hydrogen atoms for those of hydrocarbons reacting with it. Polymerisation (e.g. of hex-1-ene) may then occur as follows:



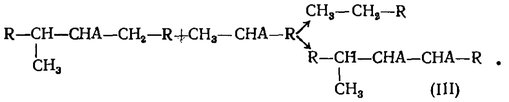
$$\mathrm{CH_2{=}CHR + HA \rightarrow \underset{(I)}{CH_3CHA{-}R}}$$

$$\mathrm{H_3C{-}CHAR + CH_2{=}CH{-}R \rightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CHR + HA}\ ,$$

which is fully analogous to Butlerov polymerisation. The dimer then reacts again with the catalyst:

$$\mathrm{R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH{-}R + HA \rightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CHA{-}CH_2{-}R}\qquad \mathrm{(II)}$$

Interaction between complexes (II) and (I) yields an alkane and the complex (III) containing less hydrogen:



$$\underset{\displaystyle CH_3}{R-\overset{|}{C}H}-CHA-CH_2-R+CH_3-CHA-R \begin{array}{l} \nearrow CH_3-CH_2-R \\ \searrow \underset{\displaystyle CH_3}{R-\overset{|}{C}H}-CHA-CHA-R \end{array} .$$

(III)

This process can be repeated. On the average every molecule may give three or four hydrogen molecules to saturate the monomer. This agrees with experimental results obtained by other workers[16].

Bashilov[17] made a detailed study of the hydropolymerisation of C_5-C_6 fractions in the presence of aluminosilicate catalysts. He showed experimentally that raising to 225–250°C the temperature of conversion of pentenes intensifies hydropolymerisation, and further rise in temperature strengthens cracking processes. The rate of redistribution of hydrogen atoms and of hydrogenation of the final reaction products is approximately the same with C_5 and C_6 alkenes.

The experimental results cited indicate the general theoretical importance of the hydro-dehydropolymerisation of alkenes on acid catalysts studied by Nametkin and his coworkers. The polymerisation of alkenes on such catalysts takes place by a cationic mechanism, in which the rate constant of chain growth is in practice usually incomparably smaller than that of termination or transfer. This extremely important fact has hitherto made it impossible to obtain products of high molecular weight by this mechanism. The cationic polymerisation of alkenes is therefore of practical interest for obtaining lower polymers, from dimers to oligomers having molecular masses of the order of a few hundreds or thousands. These oligomers are important in various branches of the chemical and petrochemical industries—the production of polymers, gasolines, lubricating oils and additives for them, the raw material for synthetic detergents, etc.—so that study of the general features and the peculiarities of the polymerisation of alkenes having various structures is not only of scientific but also of great practical interest. This governs the attention paid by research workers to the polymerisation of alkenes and several of their derivatives under the influence of various acidic catalysts. Despite the numerous papers that have appeared, many "blank spaces" still remain in our ideas on the mechanism of cationic polymerisation. However, the pioneering investigations of Lebedev and Nametkin have not lost their scientific significance even at the present time.

Experimental results confirming the hydro-dehydropolymerisation effect in several catalytic reactions of unsaturated hydrocarbons have been published even during recent years. Thus comparatively recently a study has been reported on the transformation of alkenes, cyclopropenes, alkadienes, and acetylene in the presence of $MoO_3 + Al_2O_3$.[18] The author pointed out the self-hydrogenation effects of accompanying processes of oligomerisation and isomerisation. He established that appreciable quantities of more saturated compounds than the initial hydrocarbon are formed: thus alkenes and cyclopropenes yield alkanes. The considerable quantity of hydrogen formed and of hydrogenation products found among the reaction products is regarded as indicating that the initial hydrocarbons undergo dehydrogenation on the catalyst surface followed by hydrogenation of the resulting unsaturated polymerisation products.

The experimental results are satisfactorily explained by the suggested scheme comprising—1. Dissociative adsorption of propene

$$C_3H_6\ (gas) \to C_3H_6\ (ads)\ .$$

2. Hydrogenation of propene

$$C_3H_6(ads) \xrightarrow{+H(ads)} C_3H_7(ads) \xrightarrow{+H\ (ads)} C_3H_8\ (gas)\ \cdot$$

3. Dehydrogenation of propane (transfer of hydrogen to the gas phase)

$$C_3H_7\ (ads) + H(ads) \to C_3H_6\ (ads) + H_2(gas);\ 2H(ads) \to H_2\ (gas)\ .$$

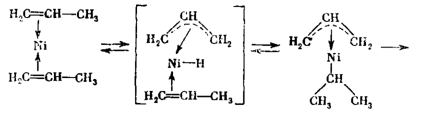
4. Formation of C_4 hydrocarbons

$$\begin{array}{ccccc} C_3H_6(ads) + CH_3\ (ads) & \to & C_4H_9(ads) & \xrightarrow{+H\ (ads)} & C_4H_{10}\ (gas) \\ +H\ (ads) \uparrow\downarrow -H\ (ads) & & -H\ (ads) \downarrow\uparrow +H\ (ads) & & \\ C_3H_5\ (ads) + CH_3(ads) & \to & C_4H_8\ (ads) & \to & C_4H_8\ (gas) \end{array}\ .$$

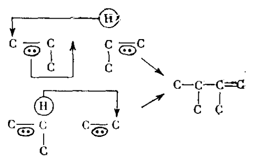
The second reaction leads to the formation of alkanes from alkenes. This may be followed by more complicated changes, in particular skeletal isomerisation. Results reported in Ref. 21 confirm and extend earlier data on the self-hydrogenation of alkenes observed in their disproportionation on $MoO_3 + Al_2O_3$ catalysts, as a consequence of which propene yields not only butene but also propane and highly unsaturated compounds.

IV. OLIGOMERISATION OF ALKENES ON TRANSITION-METAL COMPOUNDS

In all countries research workers are showing interest in the oligomerisation of alkenes on new types of catalytic systems based on compounds of transition metals. Several suggestions have been made of a reaction mechanism consisting essentially in the intramolecular transport of a hydrogen atom, i.e. with a kind of redistribution of hydrogen within the molecule. Thus in the dimerisation of propene on a complex nickel catalyst[19] the hydrocarbon undergoes oxidative addition to nickel with migration of allylic hydrogen from one propene molecule to another via an intermediate complex:



where Ni represents a coordinatively unsaturated nickel complex. Formation of a carbon–carbon σ-bond between the two coordinated alkene molecules results from activation of a carbon–hydrogen bond followed by dimerisation[18,20]:

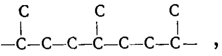


Thus the redistribution of hydrogen atoms in polymerisation processes involving alkenes on acidic catalysts, discovered by Nametkin and his coworkers, is a common phenomenon in numerous examples of the catalytic oligomerisation and polymerisation of alkenes.

V. MONOMER-ISOMERISATION POLYMERISATION ON COMPLEX ORGANOMETALLIC CATALYSTS

The discovery and the use of complex organometallic catalytic systems containing aluminium alkyls and their halogenated derivatives helped to establish fundamentally new routes to the synthesis of macromolecules of definite structure. This line of advance was reflected also in the study of the ionic–coordination polymerisation of alkenes catalysed by alkylaluminium halides. The application of these catalysts revealed new types of transformation, among which we shall discuss monomer-isomerisation polymerisation. The essence of this process is that isomerisation of the alkene precedes monomer addition. On the one hand this permits the polymerisation of alkenes having an internal double bond, previously regarded as unreactive. On the other hand, the possibility arises of undesirable isomerisation processes in the polymerisation of α-alkenes.

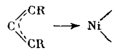
One of the first studies was made by Topchiev et al.[22] on the polymerisation of isobutene in the presence of a Ziegler type of catalyst. They discovered that the resulting polyisobutene contained fragments having the unusual structure



$$-\mathrm{C-C-\overset{C}{\overset{|}{C}}-C-C-\overset{C}{\overset{|}{C}}-C-C-\overset{C}{\overset{|}{C}}-}\ ,$$

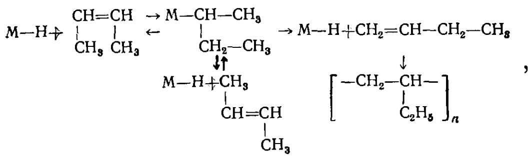
which was confirmed by numerous infrared data and also by the viscosity properties of the polymers. The occurrence of isomerisation polymerisation was suggested, but this contradicted generally accepted views on the reactivity of various cations in polymerisation processes. Unfortunately, more detailed investigations on these lines were not made, and the unusual polymerisation accompanied by formation of a polyisobutene of abnormal structure remains a matter of controversy. However, study of the polydispersity of the product by a transient sedimentation equilibrium method also showed that the structure of the polyisobutene synthesised with titanium tetrachloride plus triethylaluminium as catalyst differed from the usual polymer in a smaller degree of branching[23]. Although the polymerisation of isobutene to give the above structure is so extraordinary and improbable, the Reviewer feels that the problem is worthy of attention.

Monomer-isomerisation polymerisation[24] has been and continues to be the subject of many studies. Japanese and French workers have shown[25-32] that in many cases poly-α-alkenes can be obtained by the ionic polymerisation of β-alkenes in the presence of complex organometallic catalysts. But-2-ene was among the first β-alkenes on which monomer-isomerisation polymerisation was studied, in the presence of several catalytic systems [of which the most active comprised triethylaluminium and nickel(II) chloride] in a polar solvent, in particular pyridine. The reaction converted but-2-ene into polybut-1-ene, which was explained by isomerisation of the alkene via intermediate formation of a complex with the transition-metal compound[30-32]:



The isomerisation of alkenes having internal bonds on catalytic systems comprising an aluminium alkyl and a transition-metal compound was shown independently in experiments on several β-deuterated homologues of ethylene[33-35]. The results were interpreted on the hypothesis that two types of active centres appeared on the surface of the catalytic complex: some centres effected isomerisation of the β-alkene into an α-alkene, and the already isomerised alkene underwent polymerisation on other centres.

A reaction scheme was suggested for β-butenes as example:



where M = Al, Ni. It must be noted that isomerisation is not observed with branched alkenes.

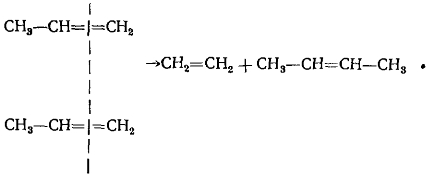
In spite of the large number of published investigations, the primary steps in a polymerisation process of this kind are still far from clear, and further detailed research is required to establish the true mechanism.

The discovery of the monomer-isomerisation polymerisation of but-2-ene is not only of theoretical interest but also of substantial practical value, since it expands considerably the raw-material base for the production of polybutene, a polyalkene possessing a valuable combination of technical properties, in particular an almost complete absence of creep.

Successful results were obtained in an investigation of the monomer-isomerisation polymerisation of pent-2-ene and hex-2-ene.[36] The plausibility of the above assumption that catalytic systems effecting monomer-isomerisation polymerisation contain two types of active centres is demonstrated by the effect of special isomerising additives on catalysts that cannot effect the process under usual conditions. Thus the monomer-isomerisation polymerisation of several higher β-alkenes can be accomplished by the use of complex organometallic catalytic systems containing acetylacetonates of certain transition metals as isomerising additives[37].

Especially noteworthy is the apparently extremely hypothetical possibility of effecting a peculiar type of isomerisation polymerisation of propene to yield from this monomer a copolymer with ethylene or (in the limiting case) polyethylene itself. Such a reaction was reported at one time by some Japanese workers in a brief communication[38], but was not subsequently confirmed.

Analogous reactions have been described in the patent literature. During recent years the disproportionation of alkenes on various types of catalytic systems has been widely used. It may be assumed that, in particular on molybdenum compounds[39,40], the disproportionation of propene yields ethylene and but-2-ene:



This may be followed by monomer-isomerisation copolymerisation of these unsaturated hydrocarbons with formation of a copolymer containing ethylene and propene units. Such a hypothesis, which has already been put forward by the Reviewer[24], undoubtedly requires experimental confirmation, especially as certain publications[41,42] quite convincingly relate the disproportionation of β-alkenes with both their homopolymerisation and their copolymerisation with other alkenes. Further research on these lines should reveal the mechanism and the characteristics of such processes.

Kennedy and his coworkers made a detailed investigation of various aspects of the cationic polymerisation and copolymerisation of alkenes, in particular of isobutene and isoprene, by means of aluminium chloride; the results have been partly summarised comparatively recently[43]. Several studies have shown[44-46] that the cationic polymerisation of isobutene and other alkenes can be accomplished by means of ethylaluminium dichloride and a hydrohalic acid. An ionic mechanism is assumed for the action of this catalyst:

$$AlR_2X + HX \rightleftarrows H^+AlR_2X_2^- \quad .$$

The resulting compound attacks the monomer:

$$H^+AlR_2X_2^- + -C{=}C- \rightarrow H-C-C^+AlR_2X_2^- \quad .$$

This is followed by the actual polymerisation:

$$H-C-C^+ + C{=}C \rightarrow H-C-C-C-C^+ \rightarrow \text{Polymer} \quad .$$

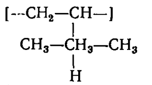
It must be noted that bimolecular protonation of the monomer is accompanied by unimolecular protonation of the gegenion. This results in formation of the saturated hydrocarbon and the corresponding aluminium dihalide:

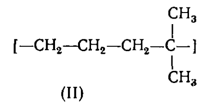
$$H^+AlR_2X_2^- \rightarrow HR + AlRX_2 \quad .$$

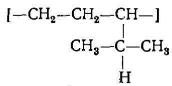
Kennedy gave[43] several experimental results on the role of such factors as the nature of the solvent in the cationic polymerisation of alkenes by means of catalytic systems based on aluminium alkyls. As was to be expected, the solvent had a significant influence both on the kinetics of polymerisation and in many cases on the structure of the polymer chain.

Saegusa et al.[47,48] made a series of interesting investigations on the cationic polymerisation of several alkenes by means of systems containing aqueous triethylalumium alone and with methoxymethyl chloride. The polymerisation was studied[49] not only of well known hydrocarbons but also of the little studied 2-methylpenta-1,3-diene, 1-isopropylindene, and 3a,4,7,7a-tetrahydroindene using catalysts of a similar type, and also paid attention to isomerisation.

Recent work by Kennedy et al.[50] has demonstrated the monomer-isomerisation polymerisation of 4-methylpent-1-ene on ethylaluminium dichloride in chloroethane at −30 to −90°C. The presence of at least the three isomeric units


(I)

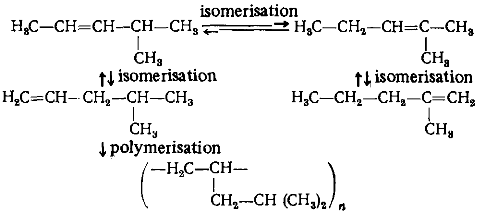

$$[-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-]$$
(II)


(III)

in the products was detected by ^{1}H n.m.r. (with a resolution of 300 MHz).

Still later publications[51,52] reported the monomer-isomerisation polymerisation (by means of catalysts of the Ziegler–Natta type) of several branched alkenes, in particular 4-methylpent-2-ene and 4-phenylbut-2-ene, as well as the copolymerisation of linear β-alkenes, of but-2-ene with pent-2-ene and of hex-2-ene. The maximum yield of the copolymer—a poly-α-alkene—reaches ~18% in the presence of triethylaluminium with vanadium or titanium trichloride as catalytic system at 80°C. The content of isomerised units in the polymer increased when the catalytic system contained nickel dimethylglyoxime or an acetylacetonate of another transition metal.

Subsequent studies by Japanese workers[53] have shown that the monomer-isomerisation polymerisation of 4-methylpent-2-ene catalysed by triethylaluminium with titanium trichloride gives a high yield of a macromolecular isotactic 4-methylpent-1-ene component. As in the preceding case, the presence in the reaction medium of acetylacetonates of transition metals, e.g. nickel acetylacetonate, increases the rate of isomerisation of the monomer. The monomer-isomerisation polymerisation of 4-methylpent-2-ene can be represented by the scheme



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The Reviewer has thus attempted to show (only on two examples) that a detailed study of the polymerisation of alkenes led to the discovery of unexpected effects, forcing a re-examination of existing views on the reaction mechanism. One such effect was discovered at the beginning of research on polymerisation as a branch of organic chemistry, and another has attracted attention during recent years in connection with the discovery of new catalytic systems and the establishment of macromolecular chemistry as an independent field of chemical science.

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Synthetic Plant Growth Regulators and Herbicides

N.N.Mel'nikov

The literature on the principal applications of various classes of inorganic and organic compounds as plant growth regulators and as agents for the suppression of weeds is briefly reviewed. The most important classes of chemical compounds employed for such purposes are quoted.
The bibliography includes 492 references.

CONTENTS

I. INTRODUCTION

The first studies on the synthesis of plant growth regulators in the Soviet Union were carried out by Nametkin as early as 1938.[1] He is justly regarded as a pioneer in this field, which is important for the national economy. Subsequent studies on these lines were continued in the laboratory organised by Nametkin at the Timiryazev Institute of Plant Physiology of the USSR Academy of Sciences; the results of this research led to the beginning of the manufacture in the USSR of preparations such as heteroauxin, 1-naphthylacetic acid, its potassium salt and methyl ether, magnesium chlorate (a defoliant), the butyl ether of 2,4-D, and certain others[2,3].

Plant growth regulators and herbicides have now found practical applications in the following principal fields[4]:

In the fight against weeds infesting a wide variety of agricultural crops, in meadows, pastures, and in forests and against undesirable plants on highways, in airports, on industrial sites, in water reservoirs, etc.[5]

In the removal of leaves prior to the harvest in order to mechanise the harvesting of the crop or in the transplanting of fruit and decorative plants and of the grapevine in order to enhance their frost resistance and increase the yield from the initial planting.

In the desiccation of plants to achieve partial drying and mechanisation of the harvesting of potatoes, rice, soya beans, and various other crops; desiccation by chemical preparations in many cases replaces the partial drying of feed crops prior to harvesting.

In the fight against the flattening of wheat, rice and other crops under conditions of increased humidity.

To increase the harvest of soya beans, peas, leguminous plants, and cotton seeds.

To increase the size of plums, pineapples, and other fruit.

To stimulate plant growth by the treatment of seeds of various crops prior to planting.[6]

To suppress the growth of young shoots to increase the intensity of flowering and fruiting of apples, pears, strawberries, and many other crops.

In the prevention of the shedding of apples and pears prior to harvesting and for the improvement of their commercial qualities and colour.

In the reduction of the strength of attachment of fruit to the stem (tomatoes, citrus fruit, etc.) for the purpose of mechanisation and in order to facilitate harvesting.

In the regulation of the metabolism of the cotton plant in order to enhance and accelerate the growth of its crop.

To increase the content of latex in rubber producing plants and to increase the content of sugar in sugar cane and sugar beet.

To accelerate the ripening of peaches and cherries.

To increase the harvest and to obtain parthenocarpic (seedless) tomatoes and other crops.

To retard the growth of tobacco shoots (chemical sucker control).

In the prevention of the germination of potatoes, onions, sugar beet, etc. on prolonged storage.

For the stimulation of the rooting of plants in their vegetative propagation by cuttings.

For the termination of the state of rest of potato tubers in order to employ them as seeding material during harvest[7].

In the destruction of male plant pollen in the cultivation of the hybrid seeds of various crops (mainly cereals).[8]

To accelerate the ripening of a number of crops.

To stimulate the opening of appleblossom and the blossom of certain other cultivated plants.

To retard the growth of lawns in order to reduce the expense of cutting.

To increase the number of internodal sections and to intensify the flowering and growth of decorative plants (chrysanthemums, azaleas, peonies, lilies, etc.).

To increase the life of cut flowers.

To stimulate the rooting of trees after transplanting.

To protect plants from the harmful action of certain herbicides.

Certain other practical applications of plant growth regulators have been described, but the studies in this field are at present in their early stages and their usefulness is not, as yet, entirely clear.

The scale of the practical applications of synthetic plant growth regulators and herbicides and the prospects for their further utilisation can be assessed from the data in Table 1,[9] which presents information on the sale of such products in the world and in the USA, expressed in terms of the 1974 prices.

Table 1. The sale of herbicides and plant growth regulators in 1971–1980.

Preparation	In the USA, million dollars			Worldwide, million dollars		
	1971	1974	1980	1971	1974	1980
Herbicides	640	1058	1523	1131	2190	3422
Plant growth regulators	18	29	40	40	77	118
Defoliants and desiccants	8	18	23	12	19	31
Total	666	1105	1586	1183	2286	3571

Evidently, chemical agents for the suppression of weeds are employed on the largest scale, which is quite understandable, since their application permits a sharp increase of labour productivity in agriculture[10]. It is sufficient to point out that, solely as a result of the expanded use of herbicides in the USA, labour productivity in agriculture increased by almost 20% from 1970 to 1974.[10] The scale of the employment of herbicides for different crops can be inferred from the data in Table 2.[9]

Table 2. The consumption of herbicides in relation to various crops (in terms of 1974 prices, million dollars).

Crop	In the USA			Worldwide		
	1971	1974	1980	1971	1974	1980
Maize	242	423	574	353	680	1061
Cotton	110	97	140	170	240	420
Wheat	40	47	71	100	200	281
Sorghum	20	33	49	28	55	81
Rice	30	23	33	106	181	309
Other grain crops	10	15	24	28	54	80
Soya beans	100	286	432	144	410	584
Tobacco	—	6	9	—	11	18
Groundnuts	14	17	24	21	32	55
Sugar beet	9	11	15	44	81	132
Other field crops	10	16	23	28	52	81
Alfalfa	5	6	9	8	16	27
Other feed crops	5	5	9	8	13	21
Meadows and pastures	15	24	36	22	40	64
Orchard crops	30	49	75	71	125	208
Fruit crops	10	19	32	29	51	86
Vegetables and potatoes	20	30	43	42	74	122
Total	640	1058	1523	1131	2190	3422

Data concerning the application of different classes of herbicidal materials are presented in Table 3,[9] which shows that the increase of the consumption of different classes of chemicals as herbicides is not uniform; the greatest increase has been in the consumption of classes of compounds which satisfy most fully modern requirements as regards selectivity of action and their influence on various objects in the environment.

The increase in consumption is greatest for new preparations, which decompose fairly rapidly in the soil and in the plant and do not leave toxic residues in the crop being protected.

In connection with the necessity for the protection of the environment, there has been an increase in the stringency of the requirements which must be met by the preparations, which significantly increases the cost of their synthesis. Data on the screening and development of new pesticides by ICI,[11] which are listed in Table 4, are interesting in this respect. Whereas in 1956 one out of 1800 compounds synthesised was subsequently manufactured on an industrial scale, in 1972 not a single preparation of the 10 000 compounds tested was manufactured industrially. In connection with the large number of biological tests, the overall period from synthesis to practical introduction into an industrial manufacturing process and agriculture lasts between 7 and 9 years.[10,11]

Table 3. The consumption of individual classes of herbicides (in terms of 1974 prices, million dollars).

Class of compounds	In the USA			Worldwide	
	1971	1974	1980	1974	1980
Arsenic compounds	8.3	11	15	27	25
Aryloxyalkanecarboxylic acids	48.2	50	65	152	260
Urea derivatives*	72.5	70	91	173	313
Carbamates and thiocarbamates**	103.0	108	120	252	363
Triazines***	340.0	314	419	620	907
Benzoic acid derivatives****	72.0	100	115	140	213
Other classes*****	413.0	405	698	826	1341

Monuron, Diuron, Phenurone, Linuron, Cotoran, and Thenoran.

**IPC, Chloro-IPC, Ordram, Tillam, Darban*, Vegadex, Avadex, Ramrod, Propanide, and Azak.

***Atrazine, Simazine, Prometon, and Prometryn.

****Amiben, Banvel-D, trichlorobenzoic acid.

*****Treflan, Paraquat, dinitrophenols, Planavin, Dynap, Solan, Herban, Lasso, Pyramin, etc.

Table 4. Results of the screening and introduction of ICI pesticides.

Type of test	1956	1964	1967	1969	1970	1972
Number of compounds screened	1800	3600	5500	5040	8000	10 000
Compounds isolated on screening	60	36	—	126	80	—
Compounds subjected to field tests	6	4	—	9	4	—
Compounds subjected to further investigation	2	2	—	2	2	—
Compounds offered for sale	1	1	1	1	1	1

Despite the high cost and considerable difficulties in the utilisation and development of new preparations, intense research is being continued in this field and new interesting herbicides and plant growth regulators appear annually, which is associated not only with the possibility of a sharp increase in labour productivity in agriculture but also with the greater economic efficiency in consequence of the considerable increase in the harvest and the improvement of the quality of agricultural produce[12-14].

An enormous number of compounds of different classes with physiological activity in plants have now been described; approximately 200 substances have found practical applications as plant growth regulators and herbicides[3-5]. Without concerning ourselves with the general theoretical problems of the nature of the action of various preparations, which have been described in fair detail in the Proceedings of the 7th International Congress[15] and in reviews and monographs[16-19], we shall consider the principal classes of chemical compounds which have found applications as plant growth regulators and herbicides in different branches of agriculture.

This review does not deal with cytokinins and gibberelins, which are described in a recent monograph in Russian.[20,21]

II. INORGANIC COMPOUNDS

Among inorganic compounds, chlorates have found fairly extensive applications as herbicides and defoliants. Potassium chlorate is used in the fight against weeds[5] and sodium, magnesium, and calcium chlorates are used to defoliate and desiccate the cotton plant and other crop plants for the purpose of the mechanisation of their harvesting[22]. In order to decrease the risk of explosion, sodium borate is added to sodium chlorate and magnesium chlorate is employed as an equilibrium mixture of sodium and magnesium chlorates and chlorides, obtained on treatment of sodium chlorate with magnesium chloride. Calcium chlorate is used as the mixture produced by treating lime with chlorine.

Among other inorganic compounds, copper compounds (nitrate and sulphate)[2,3] and ammonium sulphamate have found applications as algicides. However, the amount of ammonium sulphamate consumed per hectare is about 200 kg, which sharply reduces its use[2].

III. ALCOHOLS, PHENOLS, AND ETHERS

Allyl alcohol has found application as a herbicide[3]. C_6-C_{10} saturated alcohols are employed in sucker control for the tobacco plant[23]. Their use in combination with systematic plant growth regulators is particularly effective[24]. It is then possible to reduce the labour required for the cultivation of tobacco by more than 50%.

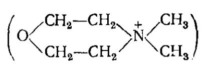
Methyl 1-naphthylmethyl ether has found application in the suppression of the germination of potato tubers on prolonged storage[3]. Derivatives of 4-nitrophenyl phenyl ether containing a wide variety of substituents in the second aromatic ring[3,5,25-34], including halogens and the trifluoromethyl and alkoxycarbonyl groups, are most widely used as herbicides in the fight against weeds infesting a wide variety of crops. These and similar compounds are obtained in high yields by the reaction of the phenoxides derived from the corresponding phenols with *p*-chloronitrobenzene and its analogues in various organic solvents and in water[35].

2-Alkyl-4,6-dinitrophenols and their esters formed with various acids, pentachlorophenol and its salts with various organic and inorganic bases[3,5], as well as 2,6-di-iodo- and 2,6-dibromo-4-cyanophenols and their salts and esters with carboxylic acids[3,5,36], known as Ioxynil and Bromoioxynil, are no less widely used as contact herbicides. These compounds are mostly employed in the fight against weeds resistant to 2,4-D preparations[3,36] in plantations of grain cereals. Ioxynil is obtained in a high yield by the iodination of 4-cyanophenol; the iodination can be also carried out electrochemically[37]. A number of other cyanophenols have been proposed as herbicides[38,39].

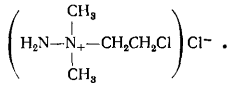
IV. AMINES AND QUATERNARY AMMONIUM SALTS

Amines and their derivatives have found fairly extensive agricultural applications in recent years and the scale of their practical utilisation is continuously increasing[3,5,9]. 2-Chloroethyltrimethylammonium chloride, known as Chlormequat, CCC, or TUR, is widely used in Europe as a plant growth regulator[40-55]. In doses ranging from 4 to 6 kg per hectare, chlormequat is used in the fight against the flattening of wheat and rice under conditions of increased humidity[40-43,45,48-51]. The application of this preparation to barley does not produce such an effect owing to the decomposition of chlormequat in the barley plants[46,47]. The application of chlormequat to wheat and rice has a major economic effect; for this reason, up to 50% of wheat plantations are treated, for example, in the German Federal Republic and in Finland. Chlormequat is used successfully on strawberries[44], vegetable cultures[46,47], in the growing of fruit[53] and cotton[54,55], and in viticulture[56]. In the growing of cotton, particularly satisfactory results have been obtained when the preparation was applied jointly with succinic acid[55].

A large number of chlormequat analogues have now been synthesised and investigated[57-76]. Some of these are highly active and may be of practical interest. In particular, trimethylalkylammonium salts containing a terpenoid structure[60,61], cyclohexyl and cyclohexenyl residues[74,75], and certain heterocyclic systems[64] in the hydrocarbon group are very active. Dimethylmorpholinium chloride (I) and 2-chloroethyldimethylhydrazinium chloride (II), and some of their analogues obtained by the reaction of alkyl halides with the corresponding amines or hydrazines[64,77,78], are of considerable interest. It is interesting to note that, when cereals are treated with 2-chloroethyldimethylhydrazinium chloride, their ripening is shortened by several days and the harvest is improved as a result of the increase of the number of sheaves. Dimethylmorpholinium chloride is active not only on wheat but also on barley, which is very significant, since in many regions barley is no less important than wheat.



(I)

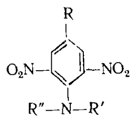


$$\left(H_2N-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N_+}}-CH_2CH_2Cl\right)Cl^- .$$

(II)

The study of the growth regulating activity of sulphur analogues of chlormequat has shown that 2-chloroethyldimethylsulphonium chloride is almost three times less active than chlormequat[64]. The corresponding quaternary pyridinium, piperidinium, pyrrolidinium, pyrazinium, tetrahydrothiophenium, thiophenium, tetrahydroxanthinium, dithianium, and azepinium salts have also been investigated, but they are all less active[64]. The introduction of a halogen into the heterocycle as a rule reduces the activity of the compound. The activity of five- and seven-membered heterocyclic compounds is significantly lower than that of compounds with six atoms in the ring. The replacement of the methyl group by others in most cases likewise leads to a decrease of the growth regulating activity[64]. Ethanolammonium salts with inorganic acids also exhibit growth regulating activity[79].

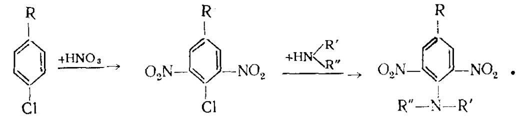
Aromatic amines have found applications as herbicides in the fight against weeds in cotton, vegetables, and many other crops[3,5,80-88]. Compounds having the general formula (III) are most widely used:



(III)

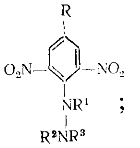
R=CH(CH$_3$)$_2$, C(CH$_3$)$_3$, CF$_3$, SO$_2$NHR, CH$_3$SO$_2$;
R′=Alk;
R″=Alk, ClCH$_2$CH$_2$.

Among the large number of compounds of this series, Treflan (2,6-dinitro-*NN*-dipropyl-4-trifluoromethylaniline) and nitraline (4-methylsulphonyl-2,6-dinitro-*NN*-dipropylaniline) are used in greatest amounts. These compounds can be obtained in high yields by the following procedure[3]:



Oryzalin (2,6-dinitro-*NN*-dipropyl-4-sulphonamidoaniline)[82,87], etafloraline [*N*-ethyl-*N*-(2-methylallyl)-2,6-dinitro-4-trifluoromethylaniline][81,88], Pregard*† (*N*-cyclo-propylmethyl-2,6-dinitro-*N*-propyl-4-trifluoromethylaniline), Dinir* (*NN*-diethyl-2,6-dinitro-*m*-phenylenediamine)[80], and certain others are being introduced into agricultural practice. The compounds of this group are not very toxic to mammals and are effective in the fight against weeds (in doses of 1–1.5 kg per hectare). However, one should note that certain compounds of this series are extremely toxic to fish[3].

One should also mention 2-hydroxyethylhydrazine, which is used in the USA to accelerate the growth of pineapples and to increase their crop[23]. It can be obtained by the reaction of oxiran and hydrazine. Among hydrazine derivatives, mention may be made of arylhydrazines having the general formula (IV)[90], which have been recommended as herbicides. These compounds are obtained similarly to the corresponding anilines:



(IV)

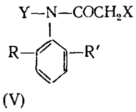
R=NH$_2$SO$_2$, CF$_3$;
R¹=H, Alk;
R², R³=Alk.

V. CARBOXYLIC ACIDS AND THEIR DERIVATIVES

One of the most important groups of compounds physiologically active in plants are carboxylic acids, among which numerous herbicides and plant growth regulators have been found. We may mention that natural plant growth regulators such as gibberellins and heteroauxins are carboxylic acid derivatives.

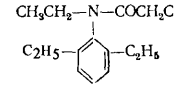
Among aliphatic compounds, derivatives of trichloroacetic, monochloroacetic, dichloropropionic, and tetrafluoropropionic acids[3] and their mixtures[89] have found extensive application as herbicides. Alkali metal trichloroacetates and dichloroprotionates are most widely used, giving satisfactory results in the fight against monocotyledonous weeds in doses of 10–50 kg per hectare[5]. Tetrafluoropropionate salts and their mixtures with dichloropropionate salts have been used successfully recently[89].

The anilides of monochloroacetic and other acids with the general formula (V)[3,91-97], which have a low toxicity for warm-blooded animals and can be used on various crops, are of considerable interest. For example, the preparation Mechet* (VI) is used successfully in the fight against weeds in rice seedlings and Anachlor* (VII) is used in plantations of maize, soya beans, groundnuts, and other crops. Propachlor (VIII), used in the fight against weeds in vegetable crops, soya beans, etc. belongs to the same group of compounds.



(V)

R, R′=Alk;
X=Cl,Br, OAr;
Y=Alk, CH$_2$OAlk



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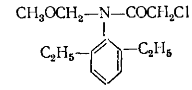
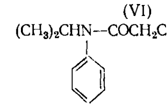
(VI)



(VII)



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(VIII)

The 3,4-dichloroanilides of propionic and other acids as well as the 3-chloro-4-methylanilides of various acids have found extensive applications in the fight against weeds in various crops. A common disadvantage of this group of compounds is their relatively high toxicity to fish and also the formation of azo-compounds as a result of their metabolism in the soil[98]. The application of compounds having the general formula (V)[99], containing the furyl and tetrahydrofuryl residues at the nitrogen atom, as well as the chloralamides [1,1,1-trichloroethylideneamides] of carboxylic acids[98] has also been patented.

Among aliphatic dibasic acid derivatives, the 2,2-dimethylhydrazide of succinic acid, known as Alar, is widely used as a plant growth regulator[100-118]. Alar is used to suppress the growth of young shoots of perennial crops, which in many instances leads to a significant increase in the crop of apples and pears harvested, reduces the shedding of the fruit prior to harvesting, improves their commercial quality, facilitates the formation of the branches of young trees, and sometimes reduces the time required for the ripening of the crop. Alar is obtained in satisfactory yields by the reaction of succinic anhydride with dimethylhydrazine. The influence of Alar on the rate of ripening of fruit and the frost resistance of apple trees[100,103,104,110] on the rate of ripening of peaches[102], morello cherries[105], and plums[106], and on the harvest of pears[107-109,112], sweet cherries[111], grapes[113], alfalfa and clover[118], carrots and tomatoes[115,117], pepper[118], brussels sprouts[119], and groundnuts has been investigated. It has been noted that Alar has a favourable influence on the majority of the crops investigated, but different types of plants respond in different ways to treatment by this preparation, so that the conditions and concentrations at which the preparation gives the optimum effect should be determined for each type of plant. Alar is usually employed at a concentration of 0.5–3 g litre^{-1}.

In the USA, Alar is used to suppress the growth of young shoots of apple and pear trees, to increase the intensity of flowering, to prevent the shedding of fruit prior to harvesting and to improve their colour, to accelerate the ripening of peaches and cherries, to increase the harvest of certain types of grapes, and to improve the flowering of azaleas and chrysanthemums. The increase in the harvest of grapes when Alar is used may be very considerable.

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†Here and henceforth the spelling of authors' names marked with an asterisk is tentative (Ed. of Translation).

Thus in some years American investigators succeeded in increasing the harvest by 25–30 centners [2500–3000 kg] per hectare[113].

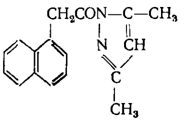
Among carboxylic acid derivatives, mention should be made of preparations which began to be used several decades ago. Such preparations include in the first place aryloxyalkanecarboxylic acids and 2-naphthylacetic acid, whose salts and amides are used to accelerate the opening of apple blossom buds and to accelerate the rooting of plants propagated by cuttings. In propagation by cuttings, the readily water-soluble salts of 2-indolylbutyric and 2-indolylacetic acids are also used[2].

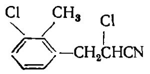
TH-656 (IX), the active principle of which is 3,5-dimethyl-1-naphthylacetylpyrazole, has been proposed to accelerate the setting of mandarin fruit[120].

2,3,6-Trichlorobenzoic, 3,6-dichloro-2-methoxybenzoic, 3-amino-2,5-dichlorobenzoic, 2,3,6-trichlorophenylacetic, and certain other acids[3,5], which are used in mixtures with other herbicides in the form of water-soluble salts formed with inorganic and organic bases, have found extensive applications as herbicides. 2,3,5-tri-iodobenzoic acid[121-125], the application of which in doses of 125–250 g per hectare increases the harvest of soya beans[121,122], alfalfa[123], peas[124], and cotton, is a plant growth regulator. However, the effectiveness of 2,3,5-tri-iodobenzoic acid depends greatly on the type of plant[121,125].

Among carboxylic acid derivatives, mention should be made of Orthonil (X) [2-(β-chloro-β-cyanoethyl)-6-chlorotoluene], the type of action of which resembles that of abscisic acid[126-128].

Tomacone* [1-(2,4-dichlorophenoxyacetyl)-3,5-dimethylpyrazole] is used to increase the harvest of tomatoes and to obtain seedless tomatoes. The water-soluble sodium salts of α-(2,4,5-trichlorophenoxy)propionic, 4-chlorophenoxyacetic, and 2-naphthoxyacetic acids are used for the same purpose. 2-Naphthoxyacetic acid is likewise employed to improve the flowering of strawberries and pineapples. *m*-Tolylphthalamic acid, which is used in the USA to improve the harvest of cherries and Lima beans, has also been applied to obtain seedless tomatoes. α-(3-Chlorophenoxy)propionic acid is used to increase the size of plums[23].


(IX)


(X)

Despite the fact that the herbicidal and plant growth regulating properties of aryloxyalkanecarboxylic acids were discovered more than 30 years ago, the study and synthesis of new derivatives of this group are still being continued[129-146]. This is quite understandable, since the scale of the manufacture and application of this group of substances is fairly large and there is no tendency towards a decrease[9,146].

The salts and esters of 2,4-dichlorophenoxyacetic, 4-chloro-2-methylphenoxyacetic, and 2,4,5-trichlorophenoxyacetic acids, the world manufacture of which has exceeded 100 000 tonnes annually, have been most widely employed[5,9,16]. The use of 2,4,5-T has been interrupted, since the technical product has been found to contain 2,3,7,8-tetrachlorodibenzo-1,4-dioxin, which is highly toxic to warm-blooded animals and man and exhibits a powerful irritant and teratogenic activity[147]. However, after the development of methods for the elimination of the above impurity, the employment of 2,4,5-T was renewed on virtually the same scale. (In most countries the rule has been adopted that the preparation must not contain more than 0.5 mg of 2,3,7,8-tetrachlorodibenzo-1,4-dioxin per kilogram.)

It has been established that the majority of the esters of the above acids exhibit a high herbicidal activity, which is proportional to the content of the corresponding acid in the ester. Furthermore, studies have been continued on the synthesis of new esters[133,140,142]: some of them are so expensive that they can hardly have practical applications. Derivatives of aryloxyalkanehydroxamic acids[138], the sugar esters of aryloxyalkanecarboxylic acids[131], derivatives of aryloxyalkanethiocarboxylic and aryloxyalkanedithiocarboxylic acids[137,143], aryloxyalkanecarboxylic acid amides[132,145], as well as aryloxyacrylic acid[135] have also been synthesised. We may note that Nametkin and his coworkers have made a significant contribution to the field of aryloxyalkanecarboxylic acids[1].

The esters formed by 1-naphthylacetic acid with poly(ethylene glycol) continue to be used for the setting of mandarin fruit[148] and unsaturated alkoxycarboxylic acid are used in the treatment of oranges[149]. Various derivatives of fluorinecarboxylic acid (XI) have found fairly extensive applications as herbicides and plant growth regulators[3,5,150-153].

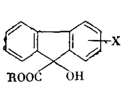
The employment of the imide of oxoglutaric acid[154] and of α-amino(hydroxyphenyl)butyric acid[155] to stimulate plant growth by treating the seeds prior to sowing has been suggested. *trans*-2-Amino-α-2-aminoethoxybutenoic acid in doses of 1–4 kg per hectare has been proposed as a herbicide to be used against beardgrass, darnel, cocklebur and other weeds.

The esters of substituted phenylpropionic acids are of interest as selective herbicides[158]; methyl α-chloro-(*p*-chlorophenyl)propionate is used in the fight against bearded oats in wheat[3,5]. It can be obtained in high yields by the following procedure[157]:

$$\mathrm{ClC_6H_4NH_2HCl} \xrightarrow{+\mathrm{HNO_2}} \mathrm{ClC_6H_4N_2Cl} \xrightarrow{+\mathrm{CH_2{=}CHCN}}$$
$$\rightarrow \mathrm{ClC_6H_4CH_2CHClCN} \xrightarrow{+\mathrm{H_2O}+\mathrm{CH_3OH}} \mathrm{ClC_6H_4CH_2CHClCOOCH_3}\ .$$

The esters of aromatic thiocarboxylic acids have also been proposed as herbicides[159].

Among carbonyl compounds, numerous aldehydes and ketones have been proposed as herbicides and plant growth regulators[160-166]. Thus C_4–C_{18} ketones have been suggested for the chemical sucker control in tobacco[160], hexahalogenoacetones have been suggested as inhibitors of the germination of potato tubers[161], and aromatic and aliphatic-aromatic ketones have been suggested as herbicides[162-165]. Both aryloxyacetophenones[166] and aminoketones[163] have been proposed as selective herbicides.

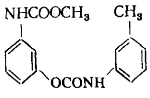

(XI)

Together with phenoxyalkanecarboxylic acids, naphthoxyalkanecarboxylic acids and their derivatives, the study of which was first began in Nametkin's laboratory[1], have been recommended in recent years for practical applications. *NN*-Diethyl-1-naphthoxy-2-propionamide, recommended as a herbicide effective against weeds in cabbage, may serve as an example of such preparations[167,168].

Among carboxylic acid derivatives, substances have been found, which are used as herbicide antidotes[169]. The anhydride of 1,8-dinaphthoic acid and the diarylamide of dichloroacetic acid may serve as examples of compounds of this kind. The latter has been fairly widely used to protect maize from damage by herbicides consisting of thiocarbamic acid derivatives. Mixtures of Eptam with diaryldichloroacetamide known as Eradicaine are nowadays used in the fight against weeds in maize plantations. Eradicaine contains 8.3% of the diallylamide of dichloroacetic acid and 91.7% of Eptam.

VI. CARBAMIC AND THIOCARBAMIC ACID DERIVATIVES

One of the fairly numerous groups of compounds with high physiological activity in plants comprises derivatives of carbamic and thiocarbamic acids[2,3]. Several decades ago, preparations such as IPC, Chloro-IPC and certain others found practical applications. During recent years, the range of arylcarbamic acid derivatives has been constantly expanding; several tens of carbamic derivatives are used at the present time[3,5,170-196]. For example, it has been found that isopropyl *N*-(3-chlorophenyl)-*N*-propoxymethylcarbamate[170], which is moderately toxic to animals, can be used as a plant growth regulator for the retardation of the growth of grasses, sucker control in tobacco, and in a number of other instances. Betanal, the active principle of which is Phenmedipham (XII)[3],



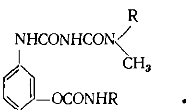
(XII)

is fairly widely used as a herbicide in the fight against weeds in sugar beet plantations. A large number of analogues of this preparation[171,182-196], including carbamic acid derivatives containing a urea residue together with the carbamoyl residue in the molecule[182,183,185,188,189,191,-192,196], have now been synthesised and proposed as herbicides. It is interesting to note that, among such derivatives, *meta*-substituted compounds exhibit the highest activity; *para*- and *ortho*-derivatives are much less physiologically active in plants.

Oxime carbamates have also been suggested as herbicides and plant growth regulators[178-181]. Thus it has been suggested that compound (XIII)[86] be used to spray orange trees in order to facilitate harvesting and that carbamoylarylenebiurets (XIV) be used as herbicides[196]:

$(C_2H_5)_2NOCONHCH_2CH_2Cl$

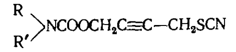
(XIII)



(XIV)

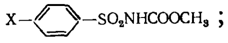
It is of interest that certain mixtures of carbamates act in the soil much longer than each component separately. For example, a 4 :1 mixture of Chloro-IPC and the 4-chlorophenyl ester of cyclohexylcarbamic acid are active for almost 14 weeks, whereas Chloro-IPC alone remains in the soil for not more than 4 weeks when used in the same doses[197].

Among the carbamic acid derivatives investigated, bifunctional derivatives containing various other functional groups apart from the carbamic acid residue have been found recently to occupy an important place[181,191,195]. In particular, compounds having the general formula (XV)[198] have been suggested as agents suitable in the fight against foxtail and compounds having the general formula (XVI) have been proposed as herbicides to combat other weeds[199].



$$\begin{matrix} R \\ R' \end{matrix}\!\!>NCOOCH_2C{\equiv}C{-}CH_2SCN$$

(XV)



(XVI) $X{=}NH_2, CH_3NH$.

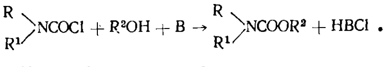
The most convenient methods for the synthesis of the alkyl and aryl esters of aryl- or alkyl-carbamic acids involve reactions of the corresponding isocyanates with alcohols or phenols[3]:

$$RNCO + R^1OH \rightarrow RNHCOOR^1$$

or of chlorocarbonates with the corresponding amines:

$$ROCOCl + NH_2R^1 \rightarrow ROCONHR^1 + HCl\ .$$

Carbamic acid esters can also be obtained by the reaction of phenols or alcohols with carbamoyl chlorides in the presence of hydrogen chloride acceptors[5]:



$$\begin{matrix} R \\ R^1 \end{matrix}\!\!>NCOCl + R^2OH + B \rightarrow \begin{matrix} R \\ R^1 \end{matrix}\!\!>NCOOR^2 + HBCl\ .$$

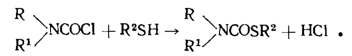
Together with carbamic acid derivatives, those of thio- and dithio-carbamic acids have found extensive applications in agriculture in the fight against weeds in various crops[3,5]. More than 15 derivatives of thiocarbamic acids, which include preparations such as Diallate, Triallate, Yalan, Tillam, Eptam, Vernolate, Sutan, Ro-Neet, Saturn and others, have now found practical applications[3,5]. Thiocarbamic acids are used in the fight against weeds in wheat, rice, maize, sugar beet, soya beans, certain vegetables and other crops. The majority of preparations of this class are introduced into the soil and then dug into a depth of 2–5 cm. The latter is necessary because of the relatively high volatility of this group of substances.

Thiocarbamic acid esters have found applications not only independently but also in mixtures with herbicide antidotes[169] and various other compounds[200]. A very large number of aliphatic, alicyclic, aromatic and heterocyclic derivatives of thiocarbamic acid have now been described; the search for new preparations belonging to this class is being vigorously continued[201-222].

Derivatives of thiocarbamic acid obtained from substituted cyclopropylamines[201], alkyleneimines[220,221], and alkyl- and dialkyl-amines, derivatives containing various substituents in the ester group[202,204], the benzyl and 2-chlorobenzyl esters of dialkylthiocarbamic acids[205,206], the 4-substituted benzyl esters of dialkylcarbamic acids[207-216], the thienylmethyl esters of dialkylthiocarbamic acids[217,-218], the pyridylalkyl esters of thiocarbamic acids[219], and many others have been described recently. Certain sulphenyl carbamates[219,223], which are the first products of the metabolism of thiocarbamic esters in the soil and other objects in the environment[223], also possess herbicidal properties.

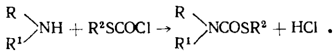
Three main procedures have been described for the preparation of various types of thiocarbamic esters[3,203,204,211,212].

The interaction of mercaptans with carbamoyl chlorides:



$$\begin{matrix} R \\ R^1 \end{matrix}\!\!>NCOCl + R^2SH \rightarrow \begin{matrix} R \\ R^1 \end{matrix}\!\!>NCOSR^2 + HCl\ .$$

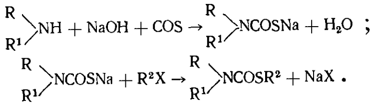
The interaction of alkyl chlorothiocarbonates with amines:



$$\begin{matrix} R \\ R^1 \end{matrix}\!\!>NH + R^2SCOCl \rightarrow \begin{matrix} R \\ R^1 \end{matrix}\!\!>NCOSR^2 + HCl\ .$$

Both reactions take place satisfactorily in the presence of hydrogen chloride acceptors.

The reaction of salts of dialkylthiocarbamic acid with alkyl halides constitutes an interesting general method for the synthesis of thiolocarbamates. The salts required are formed in high yields when amines and strong alkalis react with carbonyl sulphide:

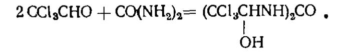


$$ {}^{R}_{R^1}{>}NH + NaOH + COS \rightarrow {}^{R}_{R^1}{>}NCOSNa + H_2O\ ; $$
$$ {}^{R}_{R^1}{>}NCOSNa + R^2X \rightarrow {}^{R}_{R^1}{>}NCOSR^2 + NaX\ . $$

II. UREA AND THIOUREA DERIVATIVES

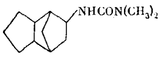
Urea and thiourea derivatives constitute one of the most portant classes of chemicals which have found fairly tensive applications in the agriculture of different coun- es[3,5,224–289]. We may note that more than 40 different phatic, alicyclic, aromatic, and heterocyclic urea erivatives are used nowadays in the fight against weeds in a wide variety of agricultural crops.

Among the aliphatic urea derivatives, we may mention dichloralurea, used in the fight against grass weeds in sugar beet and certain other crops[2]. Dichloralurea can be synthesised in high yields by the reaction between urea and chloral[290]:

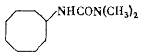


$$ 2\,CCl_3CHO + CO(NH_2)_2 = (CCl_3\underset{OH}{CH}NH)_2CO\ . $$

A number of asymmetric alicyclic ureas have been proposed as herbicides[3,252–257]; among these *NN*-dimethyl-*N'*-(perhydro-4,7-methylene-5-indanyl)urea, known under the commercial name of Herban (**XVII**), has found practical applications. This preparation is used in the fight against weeds in plantations of cotton plants, soya beans, peas, potatoes, and certain other crops in doses of 1.5–4 kg per hectare. *N*-Cyclo-octyl-*N'N'*-dimethylurea or cycluron (**XVIII**) has also found some applications[3]; it is used in plantations of beet and other vegetables in mixtures with other preparations. Other alicyclic ureas are also being investigated[252–257]:



(XVII)

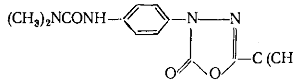


(XVIII) .

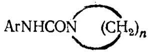
Ureas of this type are usually obtained by the reaction of the corresponding alicyclic isocyanates with amines[252–257]:

$$ RNCO + NH(CH_3)_2 \rightarrow RNHCON(CH_3)_2\ . $$

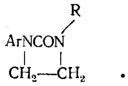
Aliphatic-aromatic derivatives of urea, some of which exhibit a highly selective action and may be used for a wide variety of crops, have found the most extensive applications. For example, 4-isopropylphenyl-*NN'*-dimethylurea has been suggested as an agent against weeds in winter wheat plantations[227,233]; 3-chloro-4-methylphenyl-*NN'*-dimethylurea[226,241] and its homologues and 3-chloro-4-methoxyphenyl-*NN*-dimethylurea and its homologues[228,234,235,239,242,245] also give satisfactory results in the fight against weeds in wheat. Cotoran [*NN*-dimethyl-*N'*-(3-trifluoromethylphenyl)urea], *N*-(3-chloro-4-trifluoromethylphenyl)-*N'N'*-dimethylurea[232], *N*-(3-chloro-4-trifluoromethoxyphenyl)-*N'N'*-dimethylurea, and certain others are widely used to combat weeds among cotton plants and other crops. Practical applications have also been suggested for *N*-(3-tetrafluoroethoxyphenyl)-*N'N'*-dimethylurea[225]. A series of urea derivatives containing various acyl groups at the nitrogen atom[236–238] as well as compounds having the general formula (**XIX**)[259–261], containing a wide variety of substituents in the aromatic group, have been proposed. Compounds having the general formulae (**XX**)[231], (**XXI**)[268], and certain others[269,270] can be classified as urea derivatives:



(XIX)

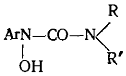


(XX)

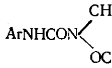


(XXI) .

Complexes of substituted ureas with acids[251] and urea derivatives of hydroxylamine[3,258] containing a hydroxy-group [compound (**XXII**)][3,181] or a methoxy-group [compound (**XXIII**)][3,258] at one of the nitrogen atoms have likewise been proposed as herbicides:

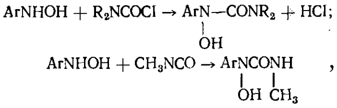


(XXII)



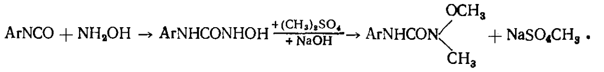
(XXIII) .

Compounds (**XXII**) are obtained in high yields by the reaction of arylhydroxylamines with dialkylcarbamoyl chlorides or alkyl isocyanates[3]:



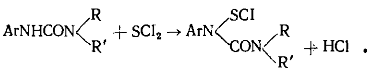
$$ ArNHOH + R_2NCOCl \rightarrow Ar\underset{OH}{N}-CONR_2 + HCl; $$
$$ ArNHOH + CH_3NCO \rightarrow Ar\underset{OH}{N}CO\underset{CH_3}{N}H\ , $$

and compounds (**XXIII**) are obtained by the following series of reactions[3]:



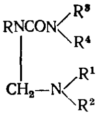
$$ ArNCO + NH_2OH \rightarrow ArNHCONHOH \xrightarrow[+NaOH]{+(CH_3)_2SO_4} ArNHCON{<}^{OCH_3}_{CH_3} + NaSO_4CH_3\ . $$

Compounds having the general formulae (**XXIV**)[244], (**XXV**), and (**XXVI**)[262–266] have been proposed recently as herbicides. Compounds (**XXV**) are obtained in high yields by the reaction of the corresponding substituted ureas with sulphur dichloride in pyridine or another similar solvent[262]:

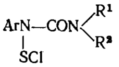


$$ ArNHCON{<}^{R}_{R'} + SCl_2 \rightarrow ArN{<}^{SCl}_{CON{<}^{R}_{R'}} + HCl\ . $$

Chlorine is readily substituted in these compounds by various other groups[263]. Compounds having the general formula (**XXVII**) have also been put forward as herbicides[246,249,253]:

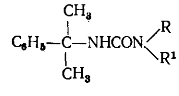


(XXIV)

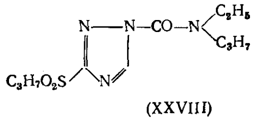


(XXV)

(XXVI)



(XXVII)



(XXVIII) .

Numerous heterocyclic ureas, including representatives of a wide variety of classes of compounds, have been suggested as agents suitable in the fight against undesirable plants. 1-(*N*-Ethyl-*N*-propylcarbamoyl)-3-propylsulphonyl-1,2,4-triazole (**XXVIII**) may serve as an example[230]. Urea herbicides include derivatives of 1,2,4-oxadiazole[287], 1,2,4-thiazole[287], furfural and pyran[275], thiazole[283,286], isothiazole[284], 1,3,4-thiadiazole[271,272,276], dichlorothiazole[278], sulphonylthiadiazole[279], pyridine[267], and certain other heterocyclic compounds[273,280-282,285,288]. Certain heterocyclic ureas have found practical applications. These include in the first place *N*-(2-benzothiazolyl)-*N'*-methylurea (Benzthiazuron), *N*-benzothiazolyl-*NN'*-dimethylurea (Metabenzthiazuron), *N*-[5-butyl-2-(1,3,4-thiadiazolyl)]-*NN'*-dimethylurea (Tebuthiuron), 1,3-dimethyl-1-[5-trifluoromethyl-2-(1,3,4-thiadiazolyl)]-urea (Thiazfluron) and others.

Despite the fact that a very large number of urea derivatives have now been described and investigated as herbicides and plant growth regulators, the research in this field is being vigorously continued and new preparations, promising for practical applications, are being systematically produced.

Certain conclusions concerning the dependence of herbicidal activity on the structure of the urea derivatives can be reached on the basis of the available data. Since this problem cannot be dealt with in detail here, we shall merely mention certain general postulates concerning substituted dialkylarylureas. Dialkylarylureas containing not more than two substituents in the benzene residue and with at least one of the *ortho*-positions relative to the amide group containing hydrogen are the most active herbicides. The total number of hydrogen atoms in the two alkyl residues at the nitrogen atom must not be more than five; in the presence of a larger number of carbon atoms in these groups, the activity of the compound falls. However, this does not apply to arylcycloalkylureas. For example, *N*-(2-methylcyclohexyl)-*N'*-phenylurea is an active herbicide. With increase of the number of carbon atoms in the alkyl or cycloalkyl residues, the overall herbicidal activity falls, but the selectivity of the action of the preparation rises.

Among *NN*-dialkyl-*N'*-arylureas, the chloro- and iodo-derivatives are the most and least active respectively. Ureas containing substituents in the 3,4-positions of the phenyl group show the most selective activity. *NN*-Dialkyl-*N'*-naphthylureas exhibit a weaker herbicidal activity. The derivatives of thiourea among which only *NN*-dimethyl-*N'*-(3-methylphenyl)thiourea has found a practical application are of lesser interest as herbicides. Other thiourea derivatives are more interesting as fungicides[3].

VIII. ORGANOPHOSPHORUS AND ORGANOARSENIC COMPOUNDS

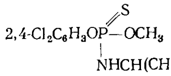
Among arsenic compounds, arsenic acid has found a practical application for the defoliation and desiccation of the cotton plant[3,22]; in the USA considerable areas of cotton plantations are treated with this substance. Salts of methylarsenic and cacodylic acids are also used in the fight against weeds. However, one should note that the wide-scale employment of arsenic in agriculture leads to its accumulation in the soil and in the plants[291]. Salts of methylarsenic and cacodylic acids have been used on a particularly large scale in mixtures with various other herbicides[289] and also in the fight against certain weeds in meadows[293].

The herbicidal and growth regulating properties of organophosphorus compounds have been investigated on a large scale during recent years and considerable advances have been achieved in this field[293-371]. Among the organophosphorus compounds investigated, there are representatives of a wide variety of phosphorus derivatives with different biological activities. The interest in organophosphorus compounds is quite understandable, since the majority of these compounds readily decompose in the soil with formation of phosphoric acid and other simple compounds, leaving practically no toxic residues in the environment[291,372]. The accumulation of organophosphorus compounds in the environment has not so far been observed[372].

Some of the first organophosphorus herbicides were the preparations Falone (**XXIX**), Zytron (**XXX**), and Prefar (**XXXI**), which have found comparatively limited applications. Butifos (**XXXII**) and Merphos (**XXXIII**) are used on a much larger scale as defoliants for the removal of leaves from the cotton plant prior to harvesting[22].

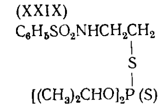
$(2,4\text{-}Cl_2C_6H_3OCH_2CH_2O)_3P$

(XXIX)



$2,4\text{-}Cl_2C_6H_3OP(=S)(-OCH_3)NHCH(CH_3)_2$

(XXX)



$C_6H_5SO_2NHCH_2CH_2\text{-}S\text{-}P(S)[OCH(CH_3)_2]_2$

(XXXI)

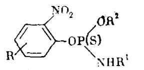
$(C_4H_9S)_3PO$

(XXXII)

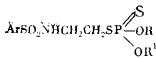
$(C_4H_9S)_3P$

(XXXIII)

A large number of Zytron analogues containing the nitro-group in the 2-position of the phenyl substituent have been synthesised recently[333,340,344,352,367,368,370,374]; compounds of this type, having the general formula (**XXXIV**), are at present being investigated in Japan under experimental industrial conditions.



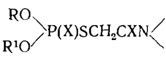
(XXXIV)



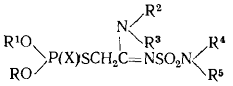
$ArSO_2NHCH_2CH_2SP(=S)(OR)OR^1$

(XXXV)

Together with the synthesis and study of a large number of Prefar analogues having the general formula (**XXXV**)[347], numerous compounds having the general formula (**XXXVI**)[332,335,345,351] and containing aliphatic[357], aromatic[351] and heterocyclic[345] residues at the nitrogen atom, have been synthesised. In most instances, these compounds exhibit selective herbicidal activity; among them, there are derivatives of both phosphorothioic and phosphorodithioic acids[332].



(XXXVI)



(XXXVII)

Prefar and its analogues can be synthesised by the following procedure[347]:

$$ArSO_2NHCH_2CH_2Cl + NaSP(S)(OR)_2 \rightarrow (RO)_2P(S)SCH_2CH_2NHSO_2Ar + NaCl.$$

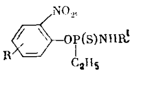
A number of other phosphates[326], phosphorothioates[349,350,359,360], phosphoramidates, and phosphoramidothioates[327,328] have been synthesised and their herbicidal and growth regulating properties investigated. For example, *SS*-dialkyl phosphorochloridodithioates, obtained by the reaction of dialkyl disulphides with phosphorus trichloride in the presence of anhydrous aluminium chloride, have been proposed as defoliants[348], while phosphorus-containing derivatives of *s*-triazine[346] and 2,3,6-trichlorobenzoylphosphazo-*N*-aryliminotrichloroacyl[338] have been proposed as herbicides.

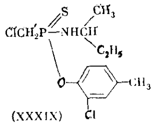
The use of phosphonate analogues of compounds (XXXIV), having the general formula (XXXVIII)[375], which are safe for the cotton plant, carrots, potatoes, and certain other crops, has been patented.

Systematic studies on the ester-amides of methylphosphonic and methylphosphonothioic acids and their derivatives, containing various substituents in the methyl group attached to the phosphorus atom, have shown that derivatives of chloromethylphosphonothioic acid exhibit the highest activity[376-379] and the ester-amides of alkylphosphonothioic acids can be arranged in the following sequence in terms of their decreasing herbicidal activity[376-379]:

$$ClCH_2{-}P > CH_3{-}P = ROCH_2{-}P > ClCH_2CH_2{-}P > C_2H_5{-}P > C_3H_7{-}P > RSCH_2{-}P > C_6H_5{-}P$$

The study of the conformational transitions of the ester-amides of chloromethylphosphonothioic acid has shown that compounds with the smallest difference between the free energies of the rotational isomers have the highest herbicidal activity[377,379]. This observation can also explain the lower herbicidal activity of phosphonates compared with phosphonothioates[377]. In this group of substances, the preparation known as Isophos-3 (XXXIX) is of considerable interest[379]:

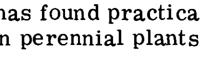

(XXXVIII)


(XXXIX)

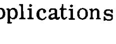
The use of Isophos-3 gives good results in the fight against weeds in rice, wheat, maize, soya beans, tomatoes, and a number of other crops. This preparation is particularly effective in the fight against millet-like weeds[379]. A large number of Isophos analogues with herbicidal activity have now been synthesised[380,381]. It is interesting to note that the ester-amides of chloromethylphosphonothioic acid containing secondary amine residues are the most active. The structure of the ester residue also has a considerable influence[379].

Phosphonomethylglycine (XL), which exhibits powerful herbicidal properties in the form of its salts with aliphatic amines, being effective against monocotyledonons perennial weeds, including witchgrass, is of great interest. This preparation, known as glyphosate, is obtained by the reaction of chloromethylphosphonic acid or its derivatives with glycine[371]. A large number of derivatives and mixtures of glyphosate with various other herbicides have been described[342,353,358,362,363].

Various carbamoylphosphonates have been proposed as growth regulators and herbicides[329,336,341,343,382], among which the ammonium salt of *O*-ethyl carbamoylphosphonic acid (XLI)[382] has found practical applications in the fight against certain perennial plants.


$(HO)_2P(=O)CH_2NHCH_2COOH$

(XL)


$C_2H_5OP(=O)(ONH_4)CONH_2$

(XLI)

2-Chloroethylphosphonic acid and some of its derivatives[292-324] (the acid is known as Ethrel, Ethephon, etc.) have found extensive applications as plant growth regulators. The action of 2-chloroethylphosphonic acid is based on the fact that, at pH > 4.5, ethylene, which possesses a high growth activating activity, is evolved. 2-Chloroethylphosphonic acid is obtained by the hydrolysis of its 2-chloroethyl ester with hydrochloric acid or hydrogen chloride[325,373,383]. Satisfactory yields are obtained when the most concentrated hydrochloric acid is employed. The 2-chloroethyl 2-chloroethylphosphonate required for synthesis is obtained in high yields by Kabachnik's method[383] from tri-(2-chloroethyl) phosphite. Together with 2-chloroethylphosphonic acid, its various derivatives[331,337,361], homologues[355,375], and many other phosphonic acid derivatives[354,366,384] have been proposed as plant growth regulators.

Depending on the concentration of the preparation and the stage of development and species of the plant, 2-chloroethylphosphonic acid can have various physiological effects: stimulation or inhibition of growth, the awakening of dormant buds, the acceleration of the ripening of fruit and vegetables, the acceleration of axillary branching of plants, the induction of flowering, the increase of frost resistance of buds, and the acceleration of the shedding of leaves, flowers, and fruit[300,301]. When Ethrel was used to vernalise wheat, an increase of the earing of the seedlings by a factor of 8–53 compared with the control seeds was noted[302]. The use of 2-chloroethylphosphonic acid on tomatoes[303-309], mandarin oranges[310,311], lemons, oranges, and grapefruits[311], peaches[312], cucumbers[313-315], cherries, onions[316], strawberries[317], hazelnuts[318], groundnuts[319], walnuts[320,321], sunflowers[322,323], tobacco[323], and the cotton plant[298] has yielded satisfactory results in the acceleration of ripening and the facilitation of the mechanisation of harvesting.

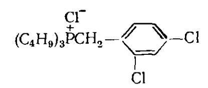
Ethrel is particularly promising for the mechanisation of the harvesting of fruit including citrus fruit. When the preparation is used, the facilitation of the removal of fruit from the plant is accompanied by the acceleration of their ripening, which promotes an increase in the harvest and an improvement in its quality. Thus peaches ripen 5 days earlier than usual[312] and the crop of tomatoes increases by 20–30%[307] and that of strawberries by 36–44%.[317] Ethrel is also an effective agent for the termination of the dormant state of groundnuts[319]. Depending on its purpose, Ethrel is used at concentrations ranging from 0.25 to 10 g litre^{-1}. It is used as a concentration of 0.5–1 g litre^{-1} as a plant growth regulator and at higher concentrations as a defoliant. Depending on the plant to be treated, its dose is 250–3000 g per hectare and the employment of even the highest concentrations of the preparation is economically justified. Ethrel leaves no toxic residues on the plants, since it decomposes almost completely with formation of phosphoric acid, which is assimilated by the plants.

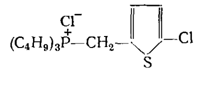
It is interesting to note that certain derivatives of 2-chloroethylsilicon[369,385] and the esters of 2-chloroethylphosphinic acid[386] have properties resembling those of Ethrel.

We may note that Ethrel is of interest also as a gametocide[387], since at concentrations of 2–3 g litre^{-1} it completely sterilises the male pollen of plants, which is of interest for the preparation of hybrid seeds.

Among phosphonic acid derivatives, mention must be made of *NN*-di(phosphonomethyl)glycine, which has been proposed for the acceleration of the ripening of sugar cane and for the increase of its sugar content[388].

Together with phosphorus acid derivatives, quaternary phosphonium salts have found practical applications in plant cultivation[293-297,365], the preparation Phosfon-D (XLII) being the best known representative of these. Phosfon-D is used as a broad-spectrum retarding agent mainly in soil under cover in relation to flowering plants. The CHE-8728 preparation [tributyl-2-chlorothienylmethylphosphonium chloride (XLIII)], recommended for increasing the crop of cotton, soya beans, kidney beans, and sugar cane, has been widely investigated recently[293–297,365]. When the above plants were sprayed with aqueous solutions of the preparation (25–30 mg litre^{-1}), the crop increased by 7–15%.


(XLII)


(XLIII)

Tributyl-2-chlorothienylmethylphosphonium chloride is obtained in high yields by the reaction of tributylphosphine with 2-chloro-5-chloromethylthiophen[365]. The tributylphosphine required for the synthesis can be obtained from tributylaluminium and phosphorus trichloride. According to patent data, trialkyl-2-chlorothienylammonium salts also possess plant growth regulating properties[334]. It is seen from the above by no means complete survey that organophosphorus compounds occupy a firm position in agriculture both as herbicides and as plant growth regulators.

IX. HETEROCYCLIC COMPOUNDS OF DIFFERENT SERIES

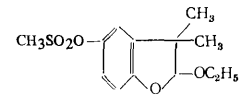
Heterocyclic compounds of different series include the greatest number of substances physiologically active in plants, which have found practical applications in agriculture[3]. Indolylacetic acid (heteroauxin) and indolylbutyric acid, which are still widely used to accelerate the rooting of plants in their vegetative propagation by cuttings[3], as well as maleic acid hydrazide, used to inhibit plant growth[391], a rational method for the manufacture of which had been developed in Nametkin's laboratory[2], have been known for the longest time.

A large number of modern herbicides are pyridine derivatives, among which the quaternary salts of 4,4'-bipyridyl and 2,2'-bipyridyl occupy the first place as regards the scale of manufacture and applications[389]; the former are obtained by the alkylation of 4,4'-bipyridyl using various alkylating agents and the latter by the reaction of dibromoethane with 2,2'-bipyridyl[389,390].

4-Amino-3,5,6-trichloropicolinic acid, which is exceptionally long acting, is a broad-spectrum herbicide[3,4].

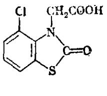
Among pyridine derivatives, we may also mention tetrachloropyridinol, dichlorodifluoropyridinol[3], the esters and other derivatives of 4-amino-3,5,6-trichloropicolinic acid[392], 3,5,6-trichloropyridylacetic acid[393], sulpho- and nitro-derivatives of chloropyridine[394–396], polychlorocyano- and dicyano-pyridines[396,397], 3,5-dichloroalkoxyethoxypyridines[398], 3,5-difluoro-2,4,6-trimethoxypyridine[399], 2-amino-6-chloro-4-trichloromethylpyridine[400], 2,3,5,6-tetrahalogeno-4-mercaptopyridines[401], polyhalogenopyridines[402–404], perchlorovinylcyanopyridine[405], halogenoalkylpyridines[406], polysubstituted dipyridylamines[407], and sulphonium derivatives of polychloropyridines[408,409], which have been proposed as plant growth regulators and herbicides. We may also note that substituted pyrrolidines[410] and maleimides[411] have been suggested as plant growth regulators.

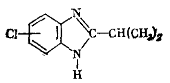
Among oxygen-containing heterocyclic compounds, 6,8-dichlorochromone[412] and various ethers of substituted hydroxytetrahydrobenzofuran[413–415] have been proposed as herbicides. In this group of preparations, 2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofurylmethanesulphonate (XLIV), known under the commercial name Nortron, is of considerable practical interest. This preparation is used in the fight against weeds in sugar beet plantations[415]. It can be obtained in high yield by the reaction of 1-ethoxy-2,3-dihydro-5-hydroxy-3,3-dimethylbenzofuran with methanesulphonyl chloride in the presence of hydrogen chloride acceptors[414]. A number of other derivatives of dihydrobenzofuran[413,414], some of which also exhibit herbicidal activity but have not so far found practical applications, can be synthesised by a similar procedure.

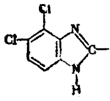

(XLIV)

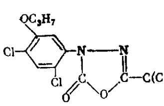
Numerous studies have been devoted to the herbicidal and plant growth regulating properties of five- and six-membered heterocyclic compounds with two heteroatoms in the ring, including derivatives of imidazoline[416,417], benzimidazoline and benzimidazole[418–420], indazole[421], pyrazole[422–425], oxazole and oxazolidine[426], thiazolidine and thiazole[427–429], isothiazole[430], hydantoin[431–434], and certain others.

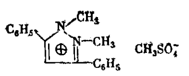
Among the classes of heterocyclic compounds enumerated above, the following have found practical applications: Benazolin (XLV), BKh-584 (XLVI), Chlorofluorazole (XLVII), RP-17623 (XLVIII), Diphensoquat* (XLIX), *NN*-dimethyl-2-(3,4,5-tribromo-1-pyrazolyl)propionamide (L), and certain others have found practical applications. Benzglycerite* (LI)[435] is a heterocyclic compound with two oxygen atoms in the ring, which has found practical applications.

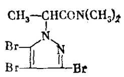

(XLV)

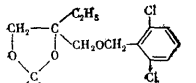

(XLVI)


(XLVII)


(XLVIII)

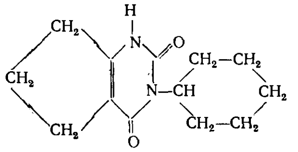

(IL)

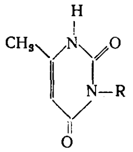

(L)


(LI)

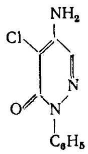
Heterocyclic compounds with two heteroatoms in the ring have found even wider practical applications. Substituted uracils[3,4,436,437], pyrimidines[438–443], and pyrazines and pyridazinones[444–453] are used on the largest scale. The most frequently used compounds of this group are Lenacil (LII) (in the fight against weeds affecting various useful plants), uracil derivatives having the general formula (LIII), Pyramin (LIV) (in the fight against weeds in sugar beet plantations), 3-phenoxypyridazine (LV), and certain others.

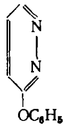
Cyclopropyl-(4-methoxyphenyl)-5-pyrimidinylmethanol (LVI) has found some applications as a plant growth regulator for the improvement of the flowering of chrysanthemums, lilies, and peonies[454]; it is employed as a spray in the form of a 0.026% solution on plants or in the treatment of soil.

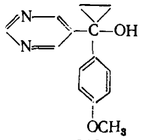

(LII)


X=Cl, Br; R=C$(CH_3)_3$, iso-C_3H_7, s-C_4H_9

(LIII)


(LIV)

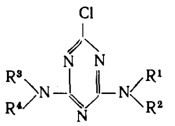

(LV)

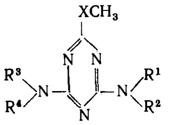

(LVI)

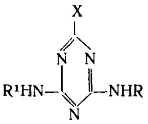
A large number of analogues of the above compounds have been synthesised and some of them may be of significant practical interest. However, their investigation has not yet been completed. There is no doubt that many interesting compounds physiologically active in plants will be found among them.

Heterocyclic compounds with three and more heteroatoms in the ring, including triazole[3], s-triazine[3,455-476] tetrahydro-s-triazine[479-482], asymmetric triazine[477,478,482], 2,2-dioxybenzo-2,1,3-thiadiazine[3,483], thiadiazole[485], oxadiazole[486], and others[484,487-491] have been investigated in detail.

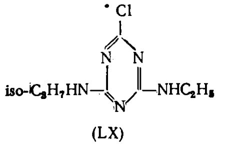
Derivatives of s-triazine, having the general formulae (LVII), (LVIII) and (LIX), which are readily obtained by the substitution of chlorine in cyanuryl chloride by the appropriate groups, have been most widely used as herbicides.

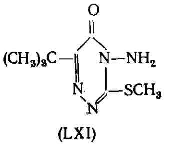

(LVII)

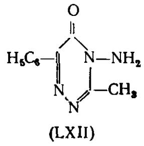

(LVIII)


(LIX)

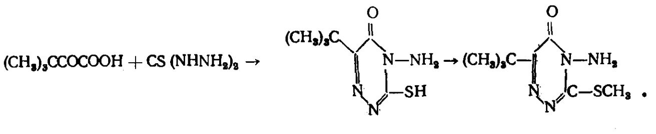
Derivatives of s-triazine occupy one of the leading places[9] among other preparations in terms of the scale of manufacture and their applications in the fight against weeds in various plantations. It is sufficient to point out that Atrazine (LX) alone is used in amounts up to 40 000 tonnes annually in the fight against weeds in maize plantations[492].


(LX)


(LXI)

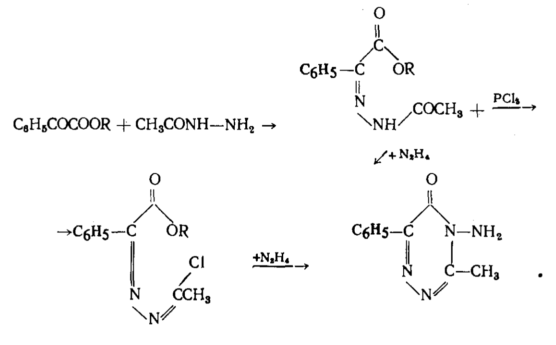

(LXII)

The first herbicide among derivatives of asymmetric thiazine is Metribuzin (Sencor) (LXI), obtained by the following procedure[477];



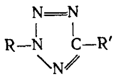
This preparation is used in the fight against weeds in soya bean, tomato, potato, and alfalfa plantations.

Another interesting preparation of this series is Metametron*[477] (LXII), obtained by the following reactions:



Metametron* has been proposed as an agent against weeds in sugar beet plantations. Particularly satisfactory results have been obtained when it was used together with certain chloroacetanilide derivatives.

Tetrazoles having the general formula (LXIII) have been proposed as plant growth regulators, inhibiting the growth of shoots and stems of various plants[489,491]:


(LXIII)

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It has not been possible to characterise fully in this review the research designed to discover and develop new chemical weed killers and plant growth regulators, but the examples quoted are sufficient to give a general idea about the scale of such studies and about the importance which chemical preparations have assumed in plant cultivation.

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†Here and henceforth the spelling of authors' names marked with an asterisk is tentative (Ed. of Translation).

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Heterogeneous Catalytic Oxidation of Aromatic Hydrocarbons in the Gas Phase

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A systematic account is given of experimental results. Kinetic data are considered from general principles based on the model of Mars and Van Krevelen supplemented by the concept of successive surface oxidation of the initial organic molecule. Certain general laws of the occurrence of reactions of this class are formulated. A list of 137 references is included.

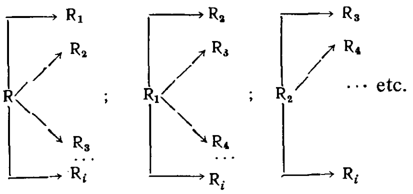
CONTENTS

I. INTRODUCTION

The heterogeneous catalytic oxidation of aromatic hydrocarbons in the gas phase includes a large number of reactions, many of practical interest. The most widely used at the present time are those yielding organic acid anhydrides (maleic, phthalic, naphthalic, trimellitic, and pyromellitic), as well as anthraquinone. The oxidation products often include other compounds of practical value—benzoquinone, naphthaquinone, aromatic aldehydes and acids, etc. In spite of the considerable variety of such reactions, their occurrence exhibits several common features, the elucidation of which should help to lay scientific foundations for the selection of catalysts.

The present Review will cover mainly work during recent years, since earlier research was the subject of a detailed discussion by Dixon and Longfield[1]. During the past fifteen years considerable improvements have been made in the experimental technique, which have permitted considerable broadening and deepening of our ideas on the kinetics and the mechanism of the oxidation of aromatic hydrocarbons. At the same time original concepts have been developed on the interrelationship between catalytic and physicochemical properties.

The oxidation of aromatic hydrocarbons usually proceeds by a consecutive–parallel mechanism. This means in general that, if a starting material R forms oxidation products R_1, R_2, ..., R_i (in order of increasing degree of oxidation), parallel processes of the type



occur, when each reaction takes place without the formation of gaseous intermediates, as well as the consecutive reactions

$$R \rightarrow R_1 \rightarrow R_2 \rightarrow R_3 \rightarrow \cdots \rightarrow R_i.$$

The complicated character of the processes creates certain difficulties in the analysis of their kinetics and mechanism, and compels recourse to various simplifications. In particular, pseudounimolecular equations are sometimes used for individual reactions in constructing a formal kinetic model, although the true kinetic relations are usually much more complex. Some authors select power formulae describing more or less satisfactorily the rates of accumulation of individual reaction products. This is in general a too crude approximation to the true kinetic equations, since the directly measurable rates of accumulation of products of mild oxidation depend on their rates of formation not only from the initial oxidisable substance but also from products of intermediate degrees of oxidation, as well as on the rate of conversion of the given reaction product into higher oxidation products. Hence such an approach is inconsistent with the consecutive–parallel character of mild oxidation established in many studies.

Definite advances in the rational interpretation of kinetic data on the basis of largely similar reaction schemes have been achieved in several recent publications. Before considering specific published information, therefore, a general discussion of such schemes and their consequences is advisable.

II. GENERALISED KINETIC MODEL OF THE CATALYTIC OXIDATION OF AROMATIC HYDROCARBONS

Mars and Van Krevelen[2,3] interpreted the kinetics of the oxidation of many substances in terms of a redox scheme involving two irreversible stages:

$$\text{Hydrocarbon R} + \text{Oxidised catalyst} \xrightarrow{r_R} \text{Oxidation products } R_1, R_2, \ldots + \text{Reduced catalyst} \quad (1)$$

$$\text{Reduced catalyst} + O_2 \xrightarrow{r_{O_2}} \text{Oxidised catalyst} . \quad (2)$$

Several workers have shown[4-8] that kinetic equations of the Langmuir–Hinshelwood type do not satisfy experimental results for the catalytic oxidation of aromatic hydrocarbons. For reactions (1) and (2) we can adopt the rate equations

$$r_R = k_R P_R \theta^a, \quad (3)$$

$$r_{O_2} = k_{O_2} P_{O_2} (1-\theta)^b, \quad (4)$$

where k_R and k_{O_2} are rate constants, θ is the coverage of the surface by oxygen, P_R and P_{O_2} are the partial pressures of the reactants, and a and b are the orders with respect to adsorbed oxygen and to oxygen vacancies on the catalyst surface respectively. In a steady state we should have

$$r_R = r_{O_2}/\nu, \tag{5}$$

where the stoichiometric coefficient ν, the number of oxygen molecules required to oxidise one R molecule to the products R_1, R_2, ..., R_i, is given by

$$\nu = \nu_1 S_1 + \nu_2 S_2 + \nu_3 S_3 + \ldots + \nu_i S_i, \tag{6}$$

in which S_i is the selectivity for R_i, and ν_i is the number of oxygen molecules involved in oxidising one R molecule to R_i. Substituting (3) and (4) in (5) yields

$$\frac{\theta^a}{(1-\theta)^b} = \frac{k_{O_2}}{k_R} \cdot \frac{1}{\nu} \cdot \frac{P_{O_2}}{P_R}, \tag{7}$$

from which it follows that the surface concentration of oxygen is a function of the ratio P_{O_2}/P_R.

For the simplest case $a = b = 1$, and from (3) and (7) we obtain for the surface coverage and the total rate of oxidation of R the formulae

$$\theta = \frac{1}{\nu} \cdot \frac{k_{O_2}}{k_R} \cdot \frac{P_{O_2}}{P_R} \Big/ \left(1 + \frac{1}{\nu} \frac{k_{O_2} P_{O_2}}{k_R P_R}\right), \tag{8}$$

$$r_R = k_{O_2} k_R P_{O_2} P_R / (k_{O_2} P_{O_2} + \nu k_R P_R). \tag{9}$$

The coefficient ν is variable, but its relative variations are often small, and for convenience a mean value $\bar{\nu}$ is used. Equation (9) can be written in a different form. For example, if the process comprises the consecutive reactions

$$R \xrightarrow[(O)]{r_R} R_1 \xrightarrow[(O)]{r_1} R_2 \xrightarrow[(O)]{r_2} R_3 \xrightarrow[(O)]{r_3} \ldots \xrightarrow[(O)]{r_{i-1}} R_i,$$

and the kinetics of each is expressed by the equation $r_i = k_i P_i \theta$, it is readily found that the overall rate of conversion of the initial substance is given by

$$r_R = \frac{k_{O_2} k_R P_{O_2} P_R}{k_{O_2} P_{O_2} + \nu_1 k_R P_R + (\nu_3 - \nu_1) k_1 P_1 + (\nu_3 - \nu_2) k_2 P_2 + \ldots + (\nu_i - \nu_{i-1}) k_{i-1} P_{i-1}}. \tag{10}$$

Since

$$S_i = (k_{i-1} P_{i-1} - k_i P_i) / k_R P_R,$$

it can be shown from (6) that

$$\nu k_R P_R = \nu_1 k_R P_R + (\nu_2 - \nu_1) k_1 P_1 + (\nu_3 - \nu_2) k_2 P_2 + \ldots + (\nu_i - \nu_{i-1}) k_{i-1} P_{i-1},$$

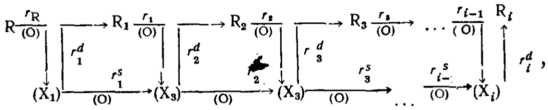
i.e. the kinetic equations (9) and (10) are equivalent.

In order to analyse the overall kinetics it is necessary to examine the detailed mechanism of the reduction stage (1). Two general schemes can be envisaged for such a mechanism. According to the first, all the observed reactions take place independently, via surface complexes specific to each reaction, e.g. on different types of active centres[9,10]. The second scheme, in contrast, is based on a close interrelationship between individual reactions. Oxidation on the surface takes place consecutively[11-16]:

$$R \xrightarrow[(O)]{} (X_1) \xrightarrow[(O)]{} (X_2) \xrightarrow[(O)]{} (X_3) \xrightarrow[(O)]{} \ldots \xrightarrow[(O)]{} (X_i)$$

(here and below parentheses denote the adsorbed state). The surface intermediates Xi yield on desorption the reaction products R_i, which may then partly undergo further oxidation. It is assumed that formation of a given product R_i involves the same final intermediate complex, independently of whether the complex has been formed from the initial compound R or by further oxidation of a product in an intermediate state of oxidation.

One variant of such a mechanism[15,16] can be represented as†



, (11)

where the r with the various affixes are the rates of the individual stages. It is evident that this scheme corresponds to a consecutive–parallel (in the generally accepted sense) reaction mechanism: the consecutive reactions are denoted by the stages

$$R \xrightarrow[(O)]{} (X_1) \rightarrow R_1 \xrightarrow[(O)]{} (X_2) \rightarrow R_2 \ldots,$$

and the parallel reactions by

$$R \xrightarrow[(O)]{} (X_1) \rightarrow R_1,\ R \xrightarrow[(O)]{} (X_1) \xrightarrow[(O)]{} (X_2) \rightarrow R_2$$

etc. Adopting for the individual stages in scheme (11) the expressions

$$r_R = k_R P_R \theta,\ r_i = k_i P_i \theta,\ r_i^d = k_i^d \theta_i,\ r_i^s = k_i^s \theta_i \theta$$

(in which the θ_i are the concentrations of the intermediate compounds X_i), we obtain for the selectivity with respect to the individual reaction products the equations[16]

$$S_1 = \frac{1}{(1 + n_1\theta)(1 + k_1\theta\tau)}, \tag{12}$$

$$S_2 = \frac{1 - S_1}{(1 + n_2\theta)(1 + k_2\theta\tau)}, \tag{13}$$

$$S_3 = \frac{1 - S_1 - S_2}{(1 + n_3\theta)(1 + k_3\theta\tau)}, \tag{14}$$

$$S_4 = \frac{1 - S_1 - S_2 - S_3}{(1 + n_4\theta)(1 + k_4\theta\tau)} \tag{15}$$

etc., where the $n_i = k_i^s/k_i^d$ are the ratios of the oxidation rate constants for the surface compounds X_i to their desorption rate constants, and τ is proportional to the contact time. In the particular case in which further oxidation of the products can be neglected and the process has a parallel mechanism (e.g. at low degrees of conversion of R), Eqns. (1)–(15) simplify to[14,15]

$$S_1 = \frac{1}{1 + n_1\theta}, \tag{16}$$

$$S_2 = \frac{1 - S_1}{1 + n_2\theta}, \tag{17}$$

$$S_3 = \frac{1 - S_1 - S_2}{1 + n_3\theta}, \tag{18}$$

$$S_4 = \frac{1 - S_1 - S_2 - S_3}{1 + n_4\theta}. \tag{19}$$

The set of equations (8), (9), and (12)–(19) describes the kinetics of all partial reactions within the framework of the given kinetic model. We can formulate certain consequences of the above ideas for the mechanism, which will then be compared with experimental results.

(1) A close analogy should exist between the catalytic reaction under steady-state conditions and the surface

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† Such a scheme is a kinetic model of a process in which the structure of intermediate complexes, their charges, etc. can be disregarded. Certain chemical aspects of the oxidation of aromatic hydrocarbons have been discussed in a review (in terms of the model of Mars and Van Krevelen)[17].

reduction of the catalyst by the initial hydrocarbon. As reduction proceeds, the surface concentration of oxygen decreases, while the selectivity for products of milder oxidation increases in conformity with Eqns. (12)–(19) with simultaneous decrease in the rate of reduction. At the same surface coverage during catalysis and reduction their rates and selectivities will also be closely similar.

(2) Selectivity during catalysis is determined by the ratio P_{O_2}/P_R of oxidant to reductant in the reaction mixture under otherwise similar conditions, since this ratio determines the surface coverage (formulae 7 and 8).

(3) Addition to the initial mixture of a product may inhibit the process, the more strongly the greater the reactivity of the compound (e.g. Eqn. 10). The Reviewer has already discussed this question in greater detail[18].

(4) In a series of catalysts of the same type a correlation should be observed between the activity and the oxygen–catalyst bonding energy q_S, analogous to that observed for complete oxidation, the mechanism of which also involves stages of alternating reduction and oxidation of the catalyst[19–21].

(5) If the variation in the rate constants of all stages in a series of catalysts is due mainly to the variation in q_S, a correlation will be observed between the selectivities S_i and q_S. Absence of such correlation may indicate that the progress of the reaction is influenced significantly by other physicochemical properties of catalysts and reactants (other than the energy of bonding of oxygen to the catalyst).

III. EXPERIMENTAL RESULTS ON THE OXIDATION OF INDIVIDUAL AROMATIC HYDROCARBONS AND THEIR OXYGEN-CONTAINING DERIVATIVES

1. Oxidation of Benzene

The catalytic oxidation of benzene to maleic anhydride (MA) is an industrial process. Low yields of phenol and *p*-benzoquinone (BQ) are also produced. The kinetics of the oxidation of benzene on the catalysts V_2O_5–K_2SO_4–SiO_2 [2,3,22] and V_2O_5–MoO_3 [23] are described by Eqn. (9).

The mechanism of the interaction of benzene with an oxide catalyst was represented[12] by the scheme

$$\begin{array}{ccccccccc} \text{Benzene} & & \text{Phenol} & & \text{BQ} & & \text{MA} & & \text{CO}_2,\text{CO} \\ \downarrow\uparrow & & \uparrow\downarrow & & \downarrow\uparrow & & \downarrow\uparrow & & \downarrow\uparrow \\ (C_6H_6) & \rightarrow & (C_6H_5OH) & \rightarrow & (C_6H_4O_2) & \rightarrow & (C_4H_3O_2) & \rightarrow & (CO_2, CO) \end{array} \quad . \qquad (20)$$

Such a scheme is consistent with experimental results showing that on separate oxidation phenol is converted into *p*-benzoquinone, maleic anhydride, and carbon dioxide[24], *p*-benzoquinone into maleic anhydride and carbon dioxide[25], and maleic anhydride into carbon dioxide[9,26]. Consecutive surface oxidation of the initial hydrocarbon forms the basis both of (20) and of scheme (11) discussed in Section II. However, the Reviewer prefers (11), since the reversible adsorption stages in (20) are inconsistent with the observed kinetics: equations like that of Mars and Van Krevelen[2,3,22,23] were deduced on the hypothesis of irreversible interaction between reactants and catalyst. The same equations, as will be shown below, agree with experimental results for other aromatic hydrocarbons and their oxygen-containing derivatives.

Several studies have been made on the effect of the chemical composition of a catalyst on its catalytic properties in the oxidation of benzene. Schaefer[27] used a microcatalytic pulse method to obtain information on the activities and selectivities of several vanadium oxides. On the assumption that unchanged activity of a specimen during an experiment indicates constancy of its chemical composition, he obtained the sequence of specific activities

$$VO_{1,99} > VO_{2,03} > VO_{2,17} > VO_{2,33} > VO_{2,50} \quad .$$

Experiments on the interaction of benzene with vanadium oxides in the absence of molecular oxygen showed[27] that the rate of catalysis exceeded the rate of reduction by factors of 1.5–7, but the sequence of the catalysts with respect to their rate of reduction by benzene was identical with the above sequence of catalytic activity.

The initial specific activities of various oxides (for degrees of conversion of benzene approaching zero) decrease in the sequence[13]

$$Co_3O_4 > Mn_2O_3 > Cr_2O_3 > NiO > CuO > Fe_2O_3 > SnO_2,\ U_3O_8 > TiO_2 > V_2O_5 > ThO_2 > ZnO > Bi_2O_3 >$$
$$> Nb_2O_5 > WO_3 > ZrO_2 > MoO_3 > Ta_2O_5 > Sb_2O_4.$$

On plotting $\lg r_{sp}$[13] against q_S (for oxides for which values of the latter were known[20]), the Reviewer obtained a characteristic curve passing through a maximum (Fig. 1*a*), which indicates that the energy of bonding of oxygen to the catalyst has a significant influence on the relative variation in the activity of individual oxides[19–21].

Among the catalysts investigated[13] only three exhibit sufficiently high selectivity with respect to products of mild oxidation (among which maleic anhydride predominates), forming the sequence $V_2O_5 > MoO_3 > WO_3$. The mixed V_2O_5–MoO_3 systems used in industry are more active and more highly selective than is vanadium pentoxide. Maximum activity corresponds to specimens containing 25–30 mole % MoO_3.[12,28] The initial selectivity for maleic anhydride[12] also passes through a maximum, reaching 62% and 25 mole % MoO_3 (the corresponding selectivities on the individual vanadium and molybdenum oxides are respectively 35% and 10%).

In a series of V_2O_5–MoO_3 catalysts an antiparallel relation is observed[30] between the specific activity and the strength of bonding of oxygen to the catalyst estimated from the initial rate of reduction by hydrogen[29] and the equilibrium partial pressure of oxygen[30] by infrared spectroscopy[31]. The opposite result is obtained when the strength of bonding is estimated from the activation energy of isotopic exchange of oxygen: addition of molybdenum(VI) oxide to vanadium(V) oxide increases the strength of bonding of oxygen to the catalyst until the composition reaches ~ 25 mole % MoO_3.[32,33] The cause of this discrepancy is obscure and requires further investigation.

The mixed vanadium–molybdenum oxide catalyst surpasses in specific catalytic activity and selectivity other binary oxide systems containing molybdenum trioxide and oxides of tin, titanium, uranium, antimony, iron, and bismuth[34]. The selectivity of V_2O_5–MoO_3 catalysts is improved by additions of thallium(III), cadmium(II), silver(I),[35] and phosphorus(V)[36] oxides. This is evident from the patent literature, where V_2O_5–MoO_3–P_2O_5 catalysts are proposed alone[37–39] and with additions of bismuth(III),[40] silver(I),[41] nickel(II), and cobalt(II + III)[42] oxides.

Phosphorus pentoxide has been regarded[43] as a structure promoter, and has been reported[44] as increasing the life of a catalyst. It may also modify chemically the catalyst surface, increasing the acidity and thereby facilitating desorption of an acidic substance—maleic anhydride—in conformity with the views of Golodets[45] on the role of acid–base properties in catalytic oxidations.

2. Oxidation of Toluene

The kinetics of the oxidation of toluene on a V_2O_5–K_2SO_4–SiO_2 catalyst can be described[2,3,46] by Eqn. (9). At low degrees of conversion the oxidation products contain[46] 86% of benzaldehyde, 4% of benzoic acid, 7% of *p*-benzoquinone, and 3% of maleic anhydride, the yield of carbon dioxide being insignificant.

Trimm and Irshad[47] established a first order with respect to toluene and zero order with respect to molecular oxygen in the oxidation of toluene on a catalyst comprising molybdenum trioxide and pumice, which may be regarded as a particular case of Eqn. (9). The slow stage involves[47] interaction of toluene with surface O^{2-} ions. The main reaction product at low degrees of conversion of toluene is benzaldehyde, with conversion into carbon dioxide not exceeding 3%.

The rate of oxidation of toluene on copper(II) oxide with additions of molybdenum and tungsten oxides (on a Silit carrier) at 350–450°C is proportional to the concentration of molecular oxygen and independent of the concentration of toluene[48]. The reaction products are benzaldehyde (selectivity up to 85% with 0.6–6% conversion of toluene) and carbon dioxide.

The sequence of oxides with respect to initial specific catalytic activity in the oxidation of toluene is[49]

$$Co_3O_4>CuO>Mn_2O_3>Fe_2O_3>Cr_2O_3>U_3O_8>NiO>V_2O_5>TiO_2>ThO_2>WO_3>ZnO>SnO_2>$$
$$>MoO_3>Bi_2O_3>Ta_2O_5>Nb_2O_5>ZrO_2>Sb_2O_4.$$

The initial selectivity of these oxides for benzaldehyde decreases in the sequence[49]

$$V_2O_5>MoO_3>WO_3>U_3O_8>NiO>Sb_2O_4>Cr_2O_3>TiO_2>Fe_2O_3>Nb_2O_5>$$
$$>Mn_2O_3>CuO>Ta_2O_5>Co_3O_4>SnO_2,\ ZnO,\ ThO_2,\ ZrO_2,\ Bi_2O_3.$$

On vanadium, molybdenum, and tungsten oxides benzaldehyde is accompanied by benzoic acid. The first two of these oxides are more selective[50] than those of copper, manganese, cobalt, lead, and iron in the oxidation of toluene to benzaldehyde. The specific catalytic activity of the oxides correlates approximately with the energy of bonding of oxygen to the catalyst (Fig. 1*b*).

It was of interest to analyse the relation between the selectivity for benzaldehyde and the energy of bonding of oxygen to the catalyst surface. If the reaction mechanism is represented by scheme (II), where R denotes toluene, R_1 benzaldehyde, R_2 benzoic acid, etc., formula (16) can be used for the selectivity for benzaldehyde (initial selectivities correspond to conditions under which complete oxidation of the products can be neglected). Applying the Brønsted–Temkin relation to individual stages in (11) on the assumption that the variation in their activation energies is determined mainly by the bonding energy q_s, we obtain

$$\begin{aligned} E_R &= E_R^0 + m_R q_s, \\ E_{O_2} &= E_{O_2}^0 - m_{O_2} q_s, \\ E_i &= E_i^0 + m_i q_s, \\ E_i^s &= (E_i^s)^0 + m_i^s q_s, \\ E_i^d &= (E_i^d)^0 + m_i^d q_s, \end{aligned} \qquad (21)$$

where $m = \alpha\gamma$ (in which α is the transport coefficient and γ a coefficient proportional to the number of oxygen–catalyst bonds ruptured or formed in the given stage). The validity of formulae (21) for E_R and E_{O_2} is confirmed by the correlation found between specific activity and bonding energy.

Differentiation of S_1 (Eqn. 16) with respect to q_s yields the expression

$$\frac{dS_1}{dq_s} = \frac{1}{RT}\left[(m_1^s - m_1^d) + (m_R + m_{O_2})(1-\theta)\right]\frac{n_1\theta}{(1+n_1\theta)^2}\ . \qquad (22)$$

Il'chenko and Golodets[51,52] have shown that the formation of highly oxidised products involves cleavage of a larger number of oxygen–catalyst bonds than does the formation of products of mild oxidation, so that $m_1^s > m_1^d$. It then follows from Eqn. (22) that the dependence of S_1 on q_s should pass through a minimum. Fig. 2*a* indicates that such a relation holds approximately for oxides of transition metals. Most oxides of non-transition metals are non-selective and depart from the correlation. It will be shown below that this is observed also for the similar oxidation of *o*-xylene to *o*-tolualdehyde.

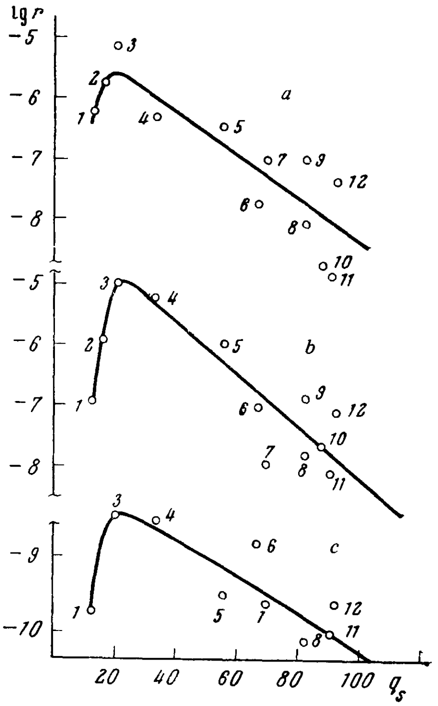


Figure 1. Dependence of lg *r* (where *r* is the reaction velocity, mole m^{-2} s^{-1}) on the oxygen–catalyst bond energy q_s (kcal g-atom^{-1} O)[20] in the oxidation of: *a*) benzene (400°C);[13] *b*) toluene (400°C);[49] *c*) *o*-xylene (300°C)[89] on the oxides: 1) NiO; 2) MnO_2 (or Mn_2O_3); 3) Co_3O_4; 4) CuO; 5) Fe_2O_3; 6) V_2O_5; 7) SnO_2; 8) ZnO; 9) U_3O_8; 10) WO_3; 11) MoO_3; 12) TiO_2.

As in the oxidation of benzene, a mixed V_2O_5–MoO_3 catalyst is more active and selective towards the oxidation of toluene than are the vanadium and molybdenum oxides separately[53]. The specific activity of binary oxide systems falls in the sequence[54]

V–Mo–O>Fe–Mo–O>Ti–Mo–O>Sb–Mo–O>U–Mo–O>Bi–Mo–O.

Among these the iron–molybdenum oxide catalyst is the most selective for benzaldehyde[54].

The poor selectivity of bismuth molybdate is explained by its great ability to accelerate not only the oxidation of methyl groups but also secondary dealkylation and degradative oxidation of toluene[55]. A selective catalyst for the oxidation of toluene to benzaldehyde is copper oxide to which tungsten and molybdenum oxides have been added, in contrast to copper oxide alone[48]. Addition of phosphorus pentoxide to molybdenum trioxide increases the activity and the selectivity for benzaldehyde, as well as the stability of the catalyst[56]. The activity of this mixed catalyst is increased by promotion with oxides of vanadium, chromium, titanium, tin, aluminium, bismuth, nickel, cobalt, and iron, while the oxidation of benzaldehyde to benzoic acid is accelerated[56]. Highly selective oxidation of toluene to benzaldehyde is achieved on a molybdenum–tungsten–aluminium oxide catalyst[57], and on molybdenum(VI) oxide with additions of vanadium(V), zirconium(IV), and copper(II) oxides on ferrochrome[58].

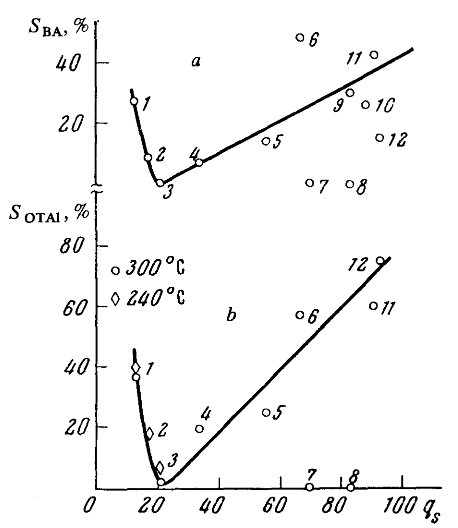


Figure 2. Dependence on q_s of the selectivity for: *a*) benzaldehyde in the oxidation of toluene (400°C)[49]; *b*) *o*-tolualdehyde in the oxidation of *o*-xylene[89]. Numbering as in Fig. 1.

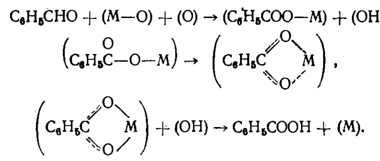
The vanadium(V)–tin(IV) oxide system is evidently highly selective, in comparison with the other catalysts studied, for the oxidation of toluene to benzoic acid[59,60]. The same system exhibits high selectivity in the oxidation of benzaldehyde to benzoic acid[61]. Results of fundamental importance for an understanding of the nature of the selective action of catalysts were also obtained[61]. The relative catalytic activity *a* and the selectivity for benzoic acid *S* of manganese dioxide, vanadium pentoxide, and the mixed catalysts were compared[61] with their thermodynamic functions—the enthalpy and the free energy ΔH and ΔF (in kcal mole^{-1}) of removal of oxygen from the oxide—Table 1, in which x is the degree of reduction of the catalyst. The antiparallel relation between catalytic activity and free energy of removal of oxygen is attributed[61] to a redox mechanism. Such a mechanism is confirmed by the close parallel between catalytic oxidation and the reduction of catalysts by benzaldehyde: at a given temperature the two processes exhibit almost the same selectivity for benzoic acid.

The suggested[61] interpretation of selective oxidation was based on certain qualitative considerations. After the adsorbed organic radical has reacted with a surface oxygen atom of the catalyst, its subsequent fate depends on the probability of (i) desorption or (ii) further chemical interaction with a neighbouring oxygen atom. Decrease in the latter probability leads to increased selectivity. This explains the increase in selectivity with the steepness of the gradient $\partial\Delta H(x)/\partial x$, since subsequent removal of a second or a third oxygen atom from the same cell requires more energy than does removal of the first atom.

Table 1.

Catalyst	$\Delta F_{x=0,02}$	$\partial\Delta H(x)/\partial x$	*a*	*S*, %
MnO_2	10	8	≫10	0
V_2–O_5–SnO_2	24	200	5	90–100
V_2O_5	38	80	1	70–80

The results obtained[61] by the kinetic method combined with infrared and electron spin resonance spectroscopy indicate for the formation of benzoic acid the detailed mechanism



$$C_6H_5CHO + (M{-}O) + (O) \rightarrow (C_6H_5COO{-}M) + (OH),$$

$$\left(C_6H_5\overset{O}{\overset{\|}{C}}{-}O{-}M\right) \rightarrow \left(C_6H_5C\langle{}^{O}_{O}\rangle M\right),$$

$$\left(C_6H_5C\langle{}^{O}_{O}\rangle M\right) + (OH) \rightarrow C_6H_5COOH + (M).$$

The reduced surface centres formed (M) are oxidised by interaction with molecular oxygen to the original oxidised state (M–O). The suggested mechanism and the hypothesis to explain selectivity evidently agree in large measure with the general mechanism expressed by scheme (11). However, energetic non-uniformity is not the only factor determining selectivity. Indeed, a diminished probability of further oxidation of the adsorbed organic complex (which is equivalent to decrease in k_i^S and hence n_i in the selectivity equations 12–19) may result from increase in the oxygen–catalyst bond energy in a series of catalysts, even if their surface oxygen is energetically equivalent.

3. Oxidation of *p*- and *m*-Xylenes

The orientation of methyl groups in *p*- and *m*-xylenes, in contrast to that in the *ortho*-isomer, does not permit formation of the very stable phthalic anhydride, so that their oxidation is considerably less selective than that of *o*-xylene. At low degrees of conversion the main products of the catalytic oxidation of the *para*- and *meta*-isomers on vanadium catalysts are *p*- and *m*-tolualdehydes and carbon dioxide (small quantities of acids are also formed)[62,63]. The formation of aldehydes and carbon dioxide proceeds by a parallel scheme[64,65].

The kinetics of the oxidation of *p*-xylene on tin vanadate[62] and on vanadium pentoxide on silica gel[64,65] is described by Eqn. (9). Increasing the reactant concentrations in the oxidation of *m*-xylene on a V_2O_5–K_2SO_4–SiO_2 catalyst[63] results in a gradual slowing down in the growth of the reaction velocity, which tends to approach a constant value; this is a characteristic feature of Mars–Van Krevelen kinetics. The main oxidation products at high degrees of conversion of *p*- and *m*-xylenes on vanadium catalysts[66] are maleic anhydride and carbon dioxide, with slight formation of aldehydes and acids.

At low degrees of conversion the oxidation of these isomers on a catalyst comprising molybdenum trioxide and pumice yields monoaldehydes and carbon dioxide[47]. The formal kinetic orders are 0.71 and 0.75 with respect to *m*- and *p*-xylenes, the corresponding values with respect to molecular oxygen being 0.40 and 0.49. The power relation is interpreted[47] as an approximation to a Langmuir–Hinshelwood type of equation.

4. Oxidation of *o*-Xylene

The oxidation of *o*-xylene to phthalic anhydride (PhA) is a promising industrial process, competing successfully with manufacture from naphthalene. This was responsible for the great interest taken by research workers in the reaction. Furthermore, many other oxidation products are obtained—*o*-tolualdehyde (oTAl), *o*-toluic acid (oTAc), phthalide (Ph), etc.—which makes the process an interesting model reaction.

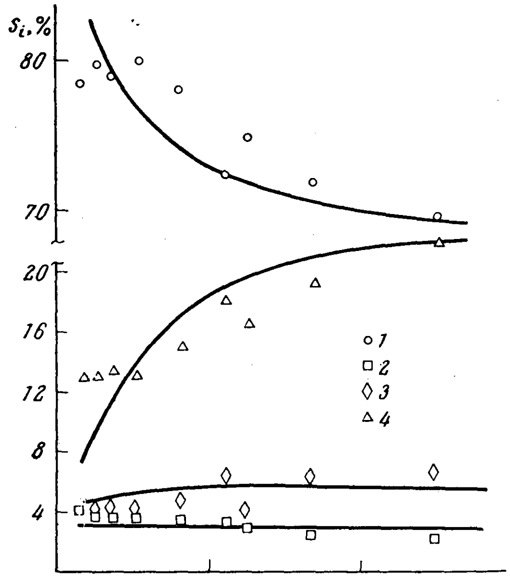


Figure 3. Dependence on the ratio P_{O_2}/P_R at 330°C of the selectivity for: 1) *o*-tolualdehyde; 2) *o*-toluic acid; 3) phthalide; 4) phthalic anhydride. The full curves have been calculated by means of Eqns. (8) and (16)–(19) with $n = 36$, $n_1 = 0.5$, $n_2 = 11$, and $n_3 = 4.5$.[15]

The mean composition of the oxidation products for low degrees of conversion (< 5 mole %) on a V_2O_5–K_2SO_4–SiO_2 catalyst at 290–310°C was 80% of *o*-tolualdehyde, 12% of *p*-benzoquinone, and 8% of carbon dioxide. The kinetics of the process was described satisfactorily by Eqn. (9), which held also for the oxidation of *o*-xylene at low degrees of conversion on fused vanadium pentoxide at 310–330°C.[6,15,67] The Mars–Van Krevelen model was used to interpret the kinetics of oxidation at high degrees of conversion on vanadium catalysts[5,68,69]. The use of other common kinetic models (the Rideal and Langmuir–Hinshelwood models) to analyse the experimental data gave negative results[4-6].

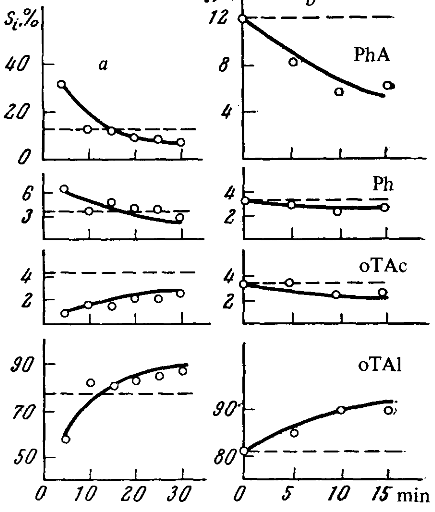
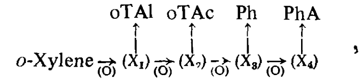


Figure 4. Dependence of selectivity on time of reduction of fused vanadium pentoxide by *o*-xylene at 330°C: *a*) catalyst specimen previously oxidised with oxygen; *b*) catalyst specimen after the catalytic oxidation of *o*-xylene under steady-state conditions[72].

Over a restricted range of conditions the kinetics of the oxidation of *o*-xylene can be described by empirical power equations[5,70,71], but such relations do not agree with experiment as well[5] as the theoretical relations based on the mechanism of Mars and Van Krevelen.

The Reviewer has used[14,15] scheme (11) to interpret the kinetics of partial reactions in the formation of individual products. In the present case this can be written



$$o\text{-Xylene} \xrightarrow[(O)]{} \overset{\substack{\text{oTAl}\\ \uparrow}}{(X_1)} \xrightarrow[(O)]{} \overset{\substack{\text{oTAc}\\ \uparrow}}{(X_2)} \xrightarrow[(O)]{} \overset{\substack{\text{Ph}\\ \uparrow}}{(X_3)} \xrightarrow[(O)]{} \overset{\substack{\text{PhA}\\ \uparrow}}{(X_4)}, \tag{23}$$

where separate experiments have demonstrated[6] that complete oxidation of the products can be neglected under the given range of conditions. Fig. 3 shows that experimental results for the selectivity with respect to all the products satisfy the theoretical relations expressed by formulae (8) and (16)–(19).

The above mechanism is supported by experimental results on the surface reduction of vanadium pentoxide by *o*-xylene[72], which takes place at about the same rate as does catalysis. The variation in selectivity on reduction agrees qualitatively with Eqns. (16)–(19) relating selectivities to surface coverage by oxygen (reduction is accompanied by decrease in θ). These results are plotted in Fig. 4 (the difference in the initial selectivities for an oxidised specimen and a specimen on which catalysis has taken place is due to a difference in the initial surface coverage, which is higher for the oxidised specimen, on which the original selectivity for more highly oxidised products is greater, in conformity with Eqns. 16–19).

The kinetics of the oxidation of *o*-xylene has been investigated[9] on a high-temperature vanadium catalyst under gradient-free conditions. The principal reactions involved were conversion of *o*-xylene into *o*-tolualdehyde, phthalic anhydride, maleic anhydride, carbon monoxide, and carbon dioxide, and of *o*-tolualdehyde into phthalic anhydride. The rates of all these reactions are represented by formulae of the same type:

$$r_{ij}=\frac{k_{ij}c_{ij}}{1+b_ic_{\mathrm{X}}+a_i(c_{\mathrm{oTAl}}+c_{\mathrm{PhA}}+c_{\mathrm{MA}})},$$

where j denotes the oxidisable compound and i the type of active centre in the catalyst, k_i, a_i, and b_i are constants, the c are concentrations, and X denotes *o*-xylene. These equations were deduced from the postulates that each reaction takes place on a separate type of active centre differing in energy of bonding of oxygen with the catalyst; the mechanism, regarded as the same for all the reactions, involved reversible adsorption of the oxidisable compound on the oxidised surface, interaction of the adsorbed molecule with surface oxygen, and desorption of the product. Reaction is inhibited by all organic components of the gas phase owing to their reversible adsorption. Oxygen vacancies are rapidly filled by oxygen from the gas phase, so that zero order with respect to molecular oxygen is observed.

Although the rate equations in Ref. 9 describe the experimental results, the physical premises underlying them are open to doubt. Thus it is not clear how the oxygen–catalyst bond energy determines unambiguously the direction in which the oxidisable substance changes.

Experimental rates of oxidation of *o*-xylene under gradient-free conditions on a vanadium catalyst have been interpreted[5] by means of a scheme according to which the hydrocarbon is converted into *o*-tolualdehyde, phthalic anhydride, and carbon dioxide, *o*-tolualdehyde into phthalic anhydride and carbon dioxide, and phthalic anhydride into carbon dioxide. The kinetic equations

$$r_i=\frac{k_iP_jk_{\mathrm{O_2}}P_{\mathrm{O_2}}}{k_{\mathrm{O_2}}P_{\mathrm{O_2}}+(k_1+k_2+k_3)P_{\mathrm{X}}+(k_4+k_5)P_{\mathrm{oTAl}}+k_6P_{\mathrm{PhA}}}$$

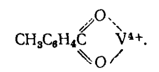
were suggested for each of these reactions, where i denotes the number of the reaction and j the oxidisable compound, k_1, k_2, and k_3 are oxidation rate constants for conversion of *o*-xylene into *o*-tolualdehyde, phthalic anhydride, and carbon dioxide respectively, k_4 and k_5 are rate constants for oxidation of *o*-tolualdehyde into phthalic anhydride and carbon dioxide, and k_6 is the rate constant of oxidation of phthalic anhydride to carbon dioxide. These equations were deduced on the hypothesis that each individual reaction occurs by irreversible interaction of the organic reactant with adsorbed oxygen at rates $k_iP_j\theta$, and that oxygen is adsorbed irreversibly at the rate $k_{\mathrm{O_2}}P_{\mathrm{O_2}}(1-\theta)$.

The agreement between the kinetic results and the above equations, together with the Arrhenius dependence of the resulting rate constants, indicates that the main features of the mechanism assumed in Ref. 5 are correct. Nevertheless, the view that individual reactions take place in isolation on the catalyst surface is in some degree artificial. A more reasonable mechanism is that represented by scheme (11), according to which the final intermediates leading to formation of a given product are the same independently of the oxidisable compound from which they had been formed. Furthermore, the above equations indicate that at low degrees of conversion the selectivity should not depend on reactant concentrations, which contradicts experiment (Fig. 3).

The close analogy between catalysis and reduction noted above suggests that the catalytic process involves surface oxygen ions O^{2-}, since it is difficult to expect other forms of oxygen, e.g. the radical-anions O^- and O_2^-, to be present on the surface during the reduction experiments. Moreover, these species are less reactive towards aromatic hydrocarbons than are other reductants (hydrogen, carbon monoxide, etc.).[73]

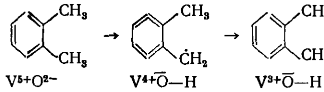
Interaction of *o*-xylene with the surface of vanadium pentoxide is accompanied by electron transfer from the hydrocarbon to the oxide[74]. Addition of small quantities of metallic palladium to the oxide accelerates significantly its reduction by *o*-xylene[75], probably because activation of carbon–hydrogen bonds is facilitated on the metal surface. The part played by additions of metals to oxides in the catalytic oxidation and reduction of the latter has been examined in detail in a review by Il'chenko[76].

With regard to the nature of the compounds X_i postulated in scheme (23) it may be suggested[72] that there is probably no significant difference in the mechanisms of formation of benzoic acid from toluene and of benzaldehyde and *o*-tolualdehyde from *o*-xylene. The structure of compound X_2 responsible for the formation of *o*-toluic acid can then be written[61]



Another acidic substance is phthalic anhydride, formed from X_4, which is most probably also saltlike in character. According to infrared-spectroscopic data[77] surface phthalates on vanadium pentoxide are readily decomposed, and can therefore be assumed to take part in the catalytic process.

We have not yet considered the mechanism of the formation of products of degradative oxidation—maleic anhydride and carbon dioxide—which may also be formed from the surface compound X_4, so that a single chain of consecutive surface reactions takes place. However, it is also possible that products of degradative oxidation are formed at least partly by a different path, when the primary attack on the hydrocarbon affects the aromatic ring. This view is held by Vanhove and Blanchard[78], who suggest that the initial interaction of *o*-xylene with a vanadium–titanium oxide catalyst in the formation of products of mild oxidation—*o*-tolualdehyde, phthalide, phthalic anhydride—follows the scheme



(reduction of the catalyst surface may involve[78] several metal ions because of the rapidity of electron transfer in the oxide lattice, so that V^{4+} ions will be formed preferentially, in agreement with experimental results). The resulting carbonium ion interacts with oxygen O^{2-} of the catalyst to give an adsorbed alkoxide ion. The latter does not undergo desorption: when a mixture of *o*-tolylmethanol and ^{14}C-labelled *o*-xylene is oxidised, the unchanged alcohol is non-radioactive. On the other hand, the alkoxide ion may serve as an intermediate species in the oxidation of *o*-xylene, since the oxidation products of *o*-tolylmethanol are also *o*-tolualdehyde, phthalide, and phthalic anhydride.

Repetition of the processes of detachment of hydrogen from the adsorbed species, electron transfer to the catalyst, and interaction with a surface oxygen ion may ultimately yield phthalic anhydride. Such is the suggested[78] mechanism of the formation of products of mild oxidation.

The degradative oxidation of *o*-xylene to maleic anhydride and oxides of carbon is attributed[78] to a competing reaction between an oxygen ion of the catalyst and the unsaturated portion of the aromatic molecule. This is consistent with results obtained by the same workers[79] on the oxidation of *o*-xylene in which a methyl group is labelled with carbon-14: the maleic anhydride detected among the reaction products is non-radioactive, so that the carboxy-groups have been formed from carbon atoms of the aromatic ring. A mechanism of formation of maleic anhydride was suggested[79] involving surface compounds of quinonoid type, which is supported by the detection of quinones among the oxidation products from *o*-xylene[4,71].

It is suggested[78] that the unsaturated part of the oxidisable molecule interacts with an oxygen ion after preliminary bonding to the catalyst as a π-complex. It is assumed also that oxidation on a series of catalysts will be more selective the weaker the bond between the π-complex and the catalyst surface.

Several studies have been made on the effect of the chemical nature of a catalyst on its activity and its selectivity in the oxidation of *o*-xylene. Investigation of the catalytic properties of individual oxides of vanadium by a pulse method showed[80] that their chemical composition changed significantly even during a short period in an atmosphere of the reaction mixture, although formation of new phases was not observed. The oxides V_2O_4, V_6O_{13}, and V_3O_7 had closely similar initial specific activities lower than that of V_2O_5 and even lower than that of V_2O_3. With increase in the number of pulses the activity and the selectivity change, abruptly with V_2O_5: after the catalytic properties of the pentoxide have been constant during the first ten pulses, the activity increases rapidly to a new constant value.

Investigation of the phase constitution of a vanadium oxide catalyst corresponding to steady-state oxidation showed[81] that, in air containing 1.1% of *o*-xylene, the catalyst comprised V_2O_5, $V_2O_{4.34}$, and V_2O_4 phases. Electron diffraction established that the $V_2O_{4.34}$ layer was located above the V_2O_4 layer. The appearance of the latter is explained in macrokinetic terms: conditions for reduction of the initial vanadium pentoxide are more severe inside the catalyst grains. With increase in the *o*-xylene concentration to 3.3 mole % the catalyst rapidly loses its activity, being converted almost completely into V_2O_4 (at the edge of the layer V_2O_3 is also detected).

The vanadium catalysts used according to the patent literature in the manufacture of phthalic anhydride from *o*-xylene can be divided into three main groups: vanadium pentoxide alone or with small quantities of additives is applied on relatively non-porous carriers (high-temperature catalysts); vanadium–potassium sulphate catalysts on carriers (silicon and titanium dioxides) resemble those employed for the oxidation of naphthalene (low-temperature catalysts); and mixed vanadium–titanium oxide catalysts (usually on an inert support) have recently found widespread application. High-temperature catalysts are not very selective, but the high temperatures permit large outputs because of the use of very short contact times[9,71,79]. The V_2O_5–K_2SO_4–SiO_2 catalysts possess enhanced selectivity, especially at low degrees of conversion, when the main product is *o*-tolualdehyde[4,63,69,71]. This applies also to vanadium–titanium oxide catalysts[82].

Investigation by Vanhove and Blanchard[82,83] of the effect of composition in the third group of catalysts indicated that specimens containing 12.5 and 89.5 mole % of titanium dioxide are initially the most selective for C_8 products. The latter specimen also possesses the maximum activity per unit mass of the catalyst. The initial selectivities correlate with the activation energies of the isotopic exchange of oxygen[83]. Increasing the degree of conversion of *o*-xylene even up to ~ 100% has little effect on the selectivity for products of degradative oxidation, mainly shifting the distribution of C_8 products towards formation of phthalic anhydride[82]. On the whole this applies also to other types of vanadium oxide catalysts[4,63,69,71,79].

Conversion of *o*-xylene into phthalic anhydride is relatively slight on tin, silver, and copper vanadates, as well as on molybdenum oxide catalysts[66]. Several studies have been made of the individual oxidation of products of the mild oxidation of *o*-xylene on vanadium catalysts[9,71,84–86]. Oxidation of *o*-tolualdehyde on the fused pentoxide[84] yields *o*-toluic acid, phthalide, phthalic anhydride, maleic anhydride, carbon monoxide, and carbon dioxide, with kinetics conforming to Eqn. (9). Power equations have been suggested[71] for the oxidation of *o*-tolualdehyde on a high-temperature vanadium catalyst and on a vanadium–potassium sulphate–silica gel catalyst. On the latter, as in the oxidation of *o*-xylene, methylbenzoquinone was formed. The oxidation of *o*-toluic acid on vanadium pentoxide at 450°C gives[85] phthalic anhydride in 85 mole % yield; the corresponding yield from *o*-xylene under analogous conditions was 67 mole %. The oxidation products from phthalide on a V_2O_5–K_2SO_4–SiO_2 catalyst are phthalic anhydride (92–95% selectivity) and carbon dioxide[71,86].

The properties of non-vanadium catalysts in the oxidation of *o*-xylene have not been adequately investigated. Popova and Kabakova[87] used copper(II) oxide with additions of molybdenum and tungsten oxides at 370–450°C. The rates of overall conversion of *o*-xylene and of formation of *o*-tolualdehyde (with ~ 15% selectivity at 380°C) and carbon dioxide are independent of the concentration of the hydrocarbon but proportional to that of molecular oxygen.

The Reviewer has obtained[88,89] initial specific activities and selectivities for the oxidation of *o*-xylene on titanium, vanadium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, tin, and chromium oxides, as well as on metallic platinum. An approximate correlation has been established between the specific activity of an oxide and the energy of bonding of oxygen (Fig. 1*c*). The specific activity of metallic platinum exceeded about thousandfold that of oxides with similar energy of bonding of oxygen, which results from the different natures of oxides and metals[19,20].

The initial selectivity for products of mild oxidation is quite high not only on typical catalysts for this process (vanadium pentoxide, molybdenum trioxide) but also on those which under normal conditions catalyse complete oxidation (Co_3O_4, MnO_2, NiO). On the cobalt oxide at 240°C, for example, the initial selectivity for phthalic anhydride is 64% (and for C_8 products 74%).

The reduction of catalysts by *o*-xylene (in experiments on cobalt and iron oxides) takes place at rates closely similar to the rate of catalysis. The gradual decrease in the rate of reduction with time is accompanied by an increase in selectivity for products of mild oxidation. Thu the rules of reduction are qualitatively the same as for vanadium pentoxide (Fig. 4).

If the oxidation of *o*-xylene takes place by mechanism (11), the dependence of the selectivity for *o*-tolualdehyde on the bonding energy for oxygen should obviously be analogous to that already discussed for the selectivity for benzaldehyde in the oxidation of toluene (Eqn. 22). This is indeed the case: an approximate correlation is observed between S_{OTAl} and q_{S} for oxides of transition metals[88,89] (Fig. 2*b*). In contrast to this, no regular relation is found between the selectivity for phthalic anhydride and the bonding energy[88,89]. One reason may be that the intermediate yielding this product may be saltlike, with its heat of desorption (also the activation energy) depending not only on q_{S} but also on the acid–base properties of the surface[45].

Results for the properties of catalysts at low degrees of oxidation both of *o*-xylene[88,89] and also of toluene[50] indicate that no sharp boundary exists under these conditions between catalysts of "complete" oxidation (cobalt, manganese, and nickel oxides) and those of "mild" oxidation (vanadium and molybdenum oxides). Differences between them are apparent with increase in the degree of conversion of the initial hydrocarbon, when further oxidation of the reaction products begins to play an appreciable part. This is accompanied on catalysts of the former type by a sharp increase in the proportion of combustion products, whereas on vanadium pentoxide further oxidation leads to a redistribution of C_8 products (with predominant formation of phthalic anhydride) and in lesser degree to an increase in the yield of products of degradative oxidation[4,63,69,71,79,82]. The resistance of phthalic anhydride to further oxidation on vanadium oxide catalysts largely determines their effectiveness.

Another factor may be that the rate of further oxidation decreases with increase in the oxygen–catalyst bond energy. However, the question then arises why the rate of oxidation of the initial hydrocarbon undergoes a greater change than do the rates of conversion of products of mild oxidation. Indeed, on the assumption that a process takes place by a consecutive scheme

$$R \xrightarrow[O_2]{r_{\mathrm{R}}} \mathrm{RO} \xrightarrow{r_{\mathrm{RO}}} \mathrm{RO_2}$$

and that

$$r_{\mathrm{R}} = k_{\mathrm{R}} P_{\mathrm{R}} \theta, \quad r_{\mathrm{RO}} = k_{\mathrm{RO}} P_{\mathrm{RO}} \theta,$$

it is easy to show that the selectivity for **RO** is

$$S_{\mathrm{RO}} = \left(1 + \frac{k_{\mathrm{RO}}}{k_{\mathrm{R}}} \frac{x}{1-x}\right)^{-1},$$

where x is the degree of conversion of the initial hydrocarbon. With different catalysts at the same degree of conversion the selectivity is evidently governed by the ratio of the reactivities of **R** and **RO**, which are measured by the rate constants k_{R} and k_{RO}. If, for example, the ratio $k_{\mathrm{RO}}/k_{\mathrm{R}}$ is independent of q_{S}, oxides having low bonding energies are more effective catalysts, since the reaction velocity on them will be higher for the same selectivity. However, experience shows that in most cases the selectivity for products of mild oxidation increases with q_{S}, including processes occurring predominantly by a consecutive scheme[90].

5. Oxidation of Acenaphthene, Pseudocumene, and Durene

As with *o*-xylene the structure of these hydrocarbons permits the formation of acid anhydrides by oxidation of methyl groups without degradation of the aromatic ring.

The oxidation of acenaphthene was investigated on vanadium pentoxide alone and with potassium sulphate, on the latter with iron and copper vanadates respectively, and on manganese dioxide (with pumice as carrier) over the range 320–450°C.[91] The chief products of mild oxidation on vanadium catalysts were acenaphthylene and naphthalic anhydride, but on manganese dioxide only acenaphthylene was formed. Increasing the ratio of air to acenaphthene tended to increase the yield of naphthalaldehyde relative to acenaphthylene (on manganese dioxide the proportion of combustion products increased). These results are qualitatively consistent with scheme (11). Oxidation of acenaphthene begins at lower temperatures on manganese dioxide than on vanadium catalysts, but the maximum yield of acenaphthylene—the product of mild oxidation—was lower on the dioxide. The yield of naphthalic anhydride reached 75–80% on the most effective of the catalysts studied[91] (iron vanadate with potassium sulphate). An active catalyst giving an 87% yield of naphthalic anhydride from acenaphthene at 355°C comprised 6% of vanadium pentoxide with 94% of titanium dioxide[92].

The oxidation of pseudocumene on vanadium pentoxide with added silver(I) and tungsten(VI) oxides at 410–420°C produces trimellitic (yield 40%), phthalic (28%), and maleic (11%) anhydrides[93]. A comparative examination of the oxidation of benzene, toluene, *o*-xylene, pseudocumene, and durene on a vanadium–molybdenum–phosphorus oxide catalyst with added sodium and nickel on synthetic corundum shows[93] that the rates of overall conversion of the alkylbenzenes are closely similar, and that the presence of isolated methyl groups in the acid anhydrides formed tends to increase the rate of production of carbon dioxide (the maximum yield of products of mild oxidation is observed with *o*-xylene). A molybdenum–tungsten oxide catalyst (1 : 9) on alundum can be used for the highly selective oxidation of pseudocumene to triformylbenzene[94].

The oxidation of durene was investigated[95-97] on fused vanadium pentoxide, the latter with additives on a carrier, V_2O_5–MoO_3–Al_2O_3, V_2O_5–SnO_2, V_2O_5–P_2O_5–kieselguhr, V_2O_5–K_2SO_4–SiO_2, V_2O_5–SnO_2–P_2O_5, V_2O_5–MnO_2–pumice, and vanadium–potassium catalysts. The best results were obtained on finely crystalline fused vanadium pentoxide: at 430–450°C with 100% conversion the yield of pyromellitic anhydride was 52–55 mole %. The fused pentoxide has been recommended also by other workers[98-100]. The yield of the anhydride is increased[101] by a considerable excess of molecular oxygen above the stoichiometric quantity. Investigation of the individual oxidation on fused vanadium pentoxide of certain products of the incomplete oxidation of durene—pyromellitic and maleic anhydrides, mono- and di-methylmaleic anhydrides, and 3-methyl-, 4-methyl-, and 4,5-dimethyl-phthalic anhydrides—showed[100,102] that the unsubstituted cyclic anhydrides were the most resistant to oxidation. The main reaction products other than oxides of carbon from the oxidation of duroquinone on fused vanadium pentoxide are dimethylmaleic anhydride and acetic acid[103]. Catalysts recommended in the patent literature for the oxidation of durene are V_2O_5–Cr_2O_3,[102] V_2O_5–MoO_3–P_2O_5 on SiC or Al_2O_3,[103] V_2O_5–WO_3–P_2O_5–Na_2O on Al_2O_3,[104] and V_2O_5–Cr_2O_3–Sb_2O_3–SnO_2 on Al_2O_3.[105] On the last catalyst the yield of pyromellitic anhydride at 360°C is 80 mole % (the temperature rises to 590°C during the process).

6. Oxidation of Naphthalene and Methylnaphthalenes

The oxidation of naphthalene on a vanadium oxide catalyst is the first industrial process for the gas-phase production of phthalic anhydride. Other products are naphthaquinone (NQ), maleic anhydride, and oxides of carbon.

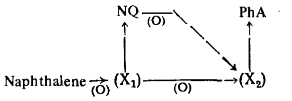
Equation (9) was suggested[2,3] to describe the kinetics of the oxidation of naphthalene on a fluidised bed of a V_2O_5–K_2SO_4–SiO_2 catalyst at 337°C. This was confirmed[106] for low degrees of conversion on the same catalyst at 300–335°C. The chief oxidation products were[106] naphtha-1,4-quinone and phthalic anhydride, with insignificant yields of maleic anhydride and carbon dioxide; naphtha-1,2-quinone was also formed (at most 5% on the content of the 1,4-quinone).

Roiter et al.[10] investigated the kinetics of the oxidation of naphthalene at 330–360°C on a V_2O_5–K_2SO_4–SiO_2 catalyst deposited on glass for degrees of conversion of naphthalene over the range 15–80% in a gradientfree reaction vessel. The equations

$$r_{PhA} = k_{PhA} P_N^0 P_{O_2},$$
$$r_{NQ} = k P_N P_{O_2} / P_{NQ}^{0.6} (1 + b P_N)$$

were suggested for the rates of formation of phthalic anhydride and naphthaquinone. The two reactions were assumed to take place in parallel, on different types of active centres[10].

The Reviewer[16] has attempted to interpret these results[10] by means of a redox model in which the reduction stage is represented by scheme (11). In the present case it can be written



(24)

The intermediate compound X_1 most probably has a quinonoid structure. The formation of such structures is indicated by electron spin resonance results obtained for the interaction of naphthalene with vanadium pentoxide[107]. The structure of X_2 can be regarded as a surface phthalate[77], as mentioned above for the mechanism of the oxidation of *o*-xylene.

The results in Ref.10 are satisfactorily described by Eqn. (9) for the total rate of the process and by Eqn. (12) for the selectivity for naphthaquinone[16]. Closely similar rate constants and activation energies of oxygen adsorption are obtained for catalysts of the same chemical composition, independently of the initial oxidisable hydrocarbon (Table 2), which supports a mechanism based on a two-stage redox model[4].

The above ideas on the mechanism are confirmed by results obtained by Andreikov et al.[108] using a pulse method for the oxidation of naphthalene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 360–380°C. Under these conditions the reaction products were naphthaquinone and phthalic anhydride; irreversible adsorption of naphthalene and its oxidation products was not observed. The composition of the initial catalyst subjected to preliminary oxidation in a stream of air at 400°C (84% V^{5+} + 16% V^{4+}) differed considerably from the steady-state composition (6% V^{5+} + 94% V^{4+}). The latter composition was independent of its mode of attainment: it was the same for preoxidised and prereduced specimens. The high degree of reduction corresponds in terms of the redox model to low surface coverage θ and hence approximately zero order with respect to naphthalene and the first order with respect to molecular oxygen, which is indeed observed experimentally[108].

Comparison of the rates of catalytic oxidation and the reduction of the V_2O_5–K_2SO_4–SiO_2 catalyst by naphthalene, as well as the selectivities of both processes[108], confirms the redox mechanism (Table 3). With increasing reduction of an oxidised catalyst specimen by naphthalene the reaction velocity gradually diminished, with a simultaneous decrease in the selectivity for phthalic anhydride from 85% to 40%. These results are consistent with scheme (24).

Table 2. Rate constants and activation energies of the adsorption of oxygen (corresponding to Eqn. 9) in the oxidation of aromatic hydrocarbons on V_2O_5–K_2SO_4–SiO_2 catalysts.

t, °C	$10^8 k_{O_2}$, moles atm^{-1} m^{-2} s^{-1}	E_{O_2}, kcal mole^{-1}	Ref.
	benzene		
350	4.7	25^{22}	22
375	9.6		
400	21.4		
	toluene		
300	0.96	29^{46}	46
325	4.8		
350	13.6		
	o-xylene		
290	0.74	26^{4}	4
300	1.08		
310	1.64		
	naphthalene		
312	1.56	28^{106}	106
335	5.3		
330	2.45	32*	*
340	4.0		
350	5.05		
360	7.25		

* Calculated from data in Ref. 16.

A similar comparison of rates of catalysis and reduction on vanadium pentoxide alone and deposited on silica revealed[109] that catalysis was rather more rapid. This was attributed[109] to partial occurrence of the reaction by an associative mechanism. The difference between the rates of catalysis and reduction diminished with rise in temperature (for 18% of the pentoxide on silica at 400°C the rates were almost identical). A similar transition to a stepwise mechanism with rise in temperature was observed[110] for other oxidations, showing that the associative mechanism involves direct participation of surface O^{2-} ions in forming the reaction products, while desorption of the products is facilitated by the presence of O_2^- radical-anions on the surface (these are absent under the conditions of the reduction experiments).

Table 3.

t, C°	Catalysis $10^5 r$, mole g^{-1} min^{-1}	S_{PhA}, %	Reduction $10^5 r$, mole g^{-1} min^{-1}	S_{PhA}, %
380	1.68	56	1.62	53
370	0.97	49	0.92	45
360	0.49	42	0.42	41

Investigation of the kinetics of the oxidation of naphthalene on vanadium pentoxide alone is complicated by changes in the chemical composition and the phase constitution of the catalyst under the influence of the reaction conditions[111]

Power rate equations were obtained[112] over a narrow range of conditions for the kinetics of the oxidation of naphthalene to individual products. The same workers[113], having taken special measures to diminish the influence of composition changes in the catalyst on the kinetics, found that the rate of formation of phthalic anhydride on coarsely crystalline vanadium pentoxide below 385°C is independent of the naphthalene concentration and proportional to the molecular oxygen concentration, but above 390°C it is proportional to the naphthalene concentration (the dependence of the rate on the oxygen concentration above 390°C was not investigated).

Equation (9) applies to the kinetics of the oxidation of 1- and 2-methylnaphthalenes on several types of vanadium–potassium sulphate–silica gel catalysts[114,115]. The mutual inhibition of the oxidation of naphthalene and methylnaphthalenes in their mixtures was explained[114,115] in terms of a redox mechanism: in the simultaneous oxidation of hydrocarbons the steady-state surface concentration of oxygen is lower than when they are oxidised separately. The rate constants of catalyst oxidation k_{O_2} are the same for different oxidisable hydrocarbons. Decrease in the degree of conversion of methylnaphthalenes[115] is accompanied by increased selectivity for the naphthaldehydes, whose yield at degrees of conversion of 35% and below exceeds the aggregate yield of the remaining products. Such "mildness" of the action of V_2O_5–K_2SO_4–SiO_2 catalysts is evident also, as noted above, in the oxidation of *o*-xylene to *o*-tolualdehyde.

An attempt was made[116,117] to examine the catalytic properties of certain individual oxides of vanadium towards the oxidation of naphthalene under pulse and continuous régimes. The composition of the specimens changed significantly even during the initial pulses (except in the case of vanadium pentoxide, on which the first pulse had hardly any influence). The specific activity sequence obtained $V_2O_{4.34} > V_2O_3 > V_2O_4 > V_2O_5$ (380–415°C) therefore relates to partly modified catalyst compositions. The extreme members of the sequence differ ninefold in specific activity, and by a factor of 13.5 in rate of formation of phthalic anhydride. Below 370°C the oxides V_2O_4 and V_2O_3 change places in the sequence. The activity and the selectivity of the pentoxide remain unchanged for ~ 1 h, in spite of the appreciable change in chemical composition, after which sharp increases are observed in the activity and in the selectivity for phthalic anhydride. Those of the other oxides remained almost unchanged for several hours' operation.

The chemical composition of the catalyst changes initially probably in its surface layers. Thus grains of fused vanadium pentoxide that had functioned in industrial plants for 2½ years were considerably reduced near the surface, whereas in the centre they remained almost unchanged[111]. The average chemical composition of separate fractions of a catalyst that had operated for a long time showed[118] a regular dependence on grain size: the content of V_2O_4 decreased from 90% to 30% between the 0.05-mm and the 0.5-mm fractions.

Vanadium–potassium sulphate systems and fused vanadium pentoxide are used in the manufacture of phthalic anhydride from naphthalene. The composite catalyst is more common though less efficient, since the selectivity for phthalic anhydride is greater thereon[119]. The properties of the mixed catalyst are improved by the continuous or periodic addition of sulphur compounds—sulphur dioxide[120–123], thionaphthen[123,124]—to the reaction mixture.

The role of potassium sulphate has not been adequately elucidated. The view has been expressed that this component diminishes the activity of vanadium pentoxide, while tending to enhance selectivity[119]. Investigation of the phase constitution and the chemical composition of vanadium–potassium sulphate systems indicates the formation of a number of chemical compounds between the pentoxide and potassium sulphate[125–127]. Study of the activity of vanadium–potassium catalysts as a function of the proportions of the components has established[128] the activity sequence

$$K_2O\cdot 4V_2O_5 > K_2O\cdot V_2O_4\cdot 8V_2O_5 > K_2O\cdot 3V_2O_5 \gg 3K_2O\cdot 5V_2O_5 > KVO_3.$$

Tin vanadate is highly active towards the oxidation of naphthalene[129]. A correlation was found[130] in the series of catalysts V_2O_5, V_2O_5–TiO_2, and V_2O_5–SnO_2 between the rate of oxidation of naphthalene and the rate of reduction of the oxides by naphthalene.

7. Oxidation of Anthracene

Anthraquinone is the main product of the oxidation of anthracene on a vanadium catalyst; phthalic anhydride is also formed. The kinetic equation (9) is applicable to oxidation on vanadium(V) oxide–potassium sulphate with iron(III) oxide[131] and with silicon dioxide[7], and on cobalt molybdate on silica gel[8]. Rate equations based on the Langmuir–Hinshelwood model were inconsistent with experimental results[8].

During operation a vanadium–potassium sulphate catalyst undergoes abrupt deactivation[132]. At 370°C this ensues after 10 h, when the degree of conversion falls from 80% to 40%, and the selectivity for anthraquinone from 90% to 40%. The deactivation was attributed[132] to the highly reduced state of the catalyst due to the great reactivity of anthracene. Additions of iron and manganese oxides to the catalytic system improve the stability of the catalyst towards reduction[133].

The chief products of the oxidation of anthraquinone on a vanadium catalyst[134] at 330–410°C are phthalic and maleic anhydrides (proportion of the latter ~ 5%) with hardly any oxides of carbon. On the same catalyst at 350°C anthraquinone is oxidised more slowly than is anthracene by factors of 30–40 and than naphtha-1,4-quinone by factors of 10–15.[134] Since anthracene is far more reactive than naphthalene, it becomes clear why selectivity for anthraquinone can be maintained at a high level far more easily than in the oxidation of naphthalene to naphthaquinone.

8. Oxidation of Phenanthrene

Kinetic investigation of the oxidation of phenanthrene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 330–370°C gave empirical power equations[132,135] for the formation of phenanthra-9,10-quinone, 9-fluorene, the lactone of 2′-hydroxybiphenyl-2-carboxylic acid, 1,2-naphthalic, phthalic, and maleic anhydrides, and carbon dioxide. The rate of oxidation of phenanthrene is less than that of anthracene on the same catalyst; deactivation of the catalyst was not observed[132].

Addition to the reaction mixture of sulphur dioxide (0.04%) improves the yield of phenanthra-9,10-quinone from 3.5% to 25% (44.7% on the phenanthrene that has reacted) in the oxidation of phenanthrene on a V_2O_5–K_2SO_4–SiO_2 catalyst at 383°C.[136]

The oxidation of phenanthrene on fused vanadium pentoxide is accompanied by significant activation of the catalyst after a few hours' operation[137].

IV. CONCLUSION

The published information surveyed, covering a large range of diverse reactions, reveals much in common in the oxidation of aromatic hydrocarbons. The consequences of the generalised kinetic model listed at the end of Section II have found confirmation in many studies. Thus the reactivity of different aromatic hydrocarbons on the same catalyst depends regularly on the energy characteristics of the oxidisable molecules (ionisation potentials[72,132], carbon–hydrogen bond energies[72]). As an example Fig. 5 illustrates the relation[72] between rate constants k_R found[4,22,46,106] by means of Eqn. (9) and the corresponding energy parameters.

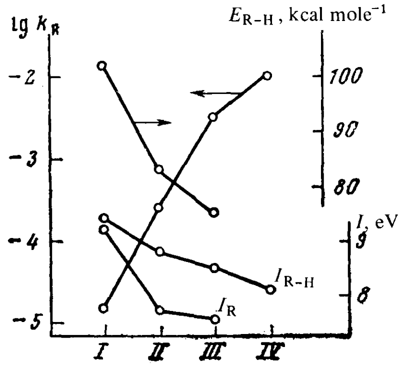


Figure 5. Variation of logarithm of rate constant k_R (with V_2O_5–K_2SO_4–SiO_2 catalyst[4,22,46,106]), R–H bond energy E_{R-H}, ionisation potential of initial molecule I_{R-H}, and ionisation potential of R· radical I_R. in a series of aromatic hydrocarbons: I) benzene; II) toluene; III) *o*-xylene; IV) naphthalene.

The above kinetic model obviously contains several simplifications. A more rigorous approach would take into account the non-uniformity of the catalyst surface. It is also possible that more than one oxygen atom is involved in individual primary stages (Eqns. (12)–(19) were deduced on the assumption that a single surface oxygen atom was involved in the oxidation stages). A further possibility is that, owing to an appreciable contribution by an associative mechanism[90,109,110], the view that the stages of reduction and oxidation of the catalyst take place independently may in individual cases (especially at low temperatures) be inadequate for interpreting the kinetic data.

Little experimental investigation has been undertaken on the reasons for the inhibiting effect sometimes exhibited by reaction products. A possible cause may be competition between oxidisable substances for available oxygen[18]. Inhibition may be due also to blocking of the surface by organic reactants. It is difficult to distinguish these two effects without detailed kinetic investigation. In many studies inhibition has been deduced from the dependence of the rates of formation of individual products on the concentration of the oxidisable substance, which is varied by changing the time of contact. Under these conditions the formal order with respect to the oxidisable substance is abnormally high, which is regarded as indicating inhibition. However, the latter may be apparent, since with increase in the period of contact not only the concentration of reaction products but also the probability of their further oxidation increases, so that the observed order may exceed the true value. In this connection it is noteworthy that, with the above experimental procedure, the formal reaction orders are always higher for products that are less oxidised and hence capable of further oxidation (independently of the nature of the initial oxidisable compound)[71,86,-111,115,132].

Vanadium catalysts—the most widely used for the oxidation of aromatic hydrocarbons—are highly active towards their degradative oxidation. Many of the products detected under mild conditions therefore undergo further transformation. However, the chain of such conversions is terminated or strongly retarded if organic acid anhydrides are formed. High yields of the latter can always be obtained if the initial oxidisable molecule contains a chain of at least four carbon atoms that includes an unsaturated bond (aromatic hydrocarbons, butenes, pentenes, heterocycles, etc.).

Anthraquinone is also comparatively resistant to oxidation on vanadium catalysts, which is responsible for its high yield from the oxidation of anthracene. Naphthaquinone and especially benzoquinone are less stable. The decrease in the yield of quinones in the sequence—anthracene, naphthalene, benzene—is intensified also by the fall in reactivity of the initial hydrocarbon in the same sequence. Formation of quinonoid structures probably precedes oxidative degradation of the aromatic ring. In the case of alkylated hydrocarbons this process competes with oxidation of the alkyl groups. This may be why, in the oxidation of *o*-xylene on vanadium catalysts, a considerable yield of oxides of carbon is observed (as noted above, benzoquinone is unstable). Intermediate formation of quinonoid structures takes place also in the oxidation of naphthalene, but, in contrast to the oxidation of *o*-xylene, they may be precursors of phthalic anhydride, which is stable towards further oxidation; and smaller quantities of carbon dioxide are obtained from naphthalene than from *o*-xylene on the same catalysts[119].

Catalysts having the same chemical composition show largely similar behaviour in the oxidation of different aromatic compounds. Thus vanadium pentoxide undergoes partial reduction during the reaction, with the formation of lower vanadium oxides as separate phases. The resulting catalyst is more active and more selective than the initial system, independently of the nature of the oxidisable aromatic hydrocarbon (benzene[27], *o*-xylene[80], naphthalene[116,-117], phenanthrene[137]). The great activity of vanadium pentoxide alone is often used to obtain a high output of a desired product of mild oxidation, despite a considerable loss of the initial hydrocarbon by combustion.

Vanadium–potassium sulphate systems are characterised by low outputs, but possess enhanced selectivity. The mildness of the action of such catalysts is especially clearly shown at not too high degrees of conversion of the oxidisable substance, when products of the mildest oxidation predominate—aldehydes from *o*-xylene[4] and methylnaphthalenes[114,115], quinones from naphthalene[10,106] and anthracene[132].

The Reviewer has enumerated certain general features of the selective catalytic oxidation of aromatic hydrocarbons in order to emphasise the interrelationship of mechanism, kinetics of various reactions, and selective action of various catalytic systems. This should facilitate future discussion of new experimental results concerning specific reactions.

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Methods for the Synthesis of Complexones—Aminopolyacetic Acids

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Methods for the synthesis of "true" complex-forming agents containing one or several iminodiacetic acid groups are examined and discussed.
The bibliography includes 203 references.

CONTENTS

I. INTRODUCTION

Among organic complex-forming agents, one of the most important places is occupied by polyaminopolyacetic acids—the so called complexones derived from iminodiacetic acid. Compounds of this series are capable of interacting with almost all metal cations, forming chelate complexes readily soluble in water. By virtue of these properties, complexones have found applications in various branches of science and engineering, agriculture, biology, and medicine.

Complexones are widely used as water softening agents[1], for example, in the leather, textile, and food industries and in photography. Complexometry[2], an analytical procedure based on the use of complexones whereby almost all metals can be determined quantitatively, has been developed extensively and is widely used in analytical chemistry. The employment of complexones for the separation of cations of elements having similar properties (particularly lanthanides) and for obtaining them in a pure form has become very important under laboratory and industrial conditions[3]. Complexones have proved to be extremely valuable in power engineering, primarily in nuclear power engineering as agents for the washing and passivation of the equipment, where they are used as such or in the form of compositions[4,5].

The ability of complexones to bind strongly heavy metal ions is used to inhibit the oxidation processes catalysed by these cations, which has served as a basis for the application of complexones as stabilisers and antioxidants, particularly in the chemical and pharmacological industries[6,7], biology, and preparative organic chemistry. The ability of complexones to form stable water-soluble complexes with metals (particularly those important for plants) led to their use as agents in the fight against chlorosis in certain agricultural crops[8]. Some complexones, for example ethylenediaminetetra-acetic and diethylenetriaminepenta-acetic acids, have found application as medicinal agents accelerating the elimination from the organism of toxic metals, including radioactive metals[9,10].

More than 30 years have elapsed since the first, parent substances of the class of complexones—nitrilotriacetic and ethylenediaminetetra-acetic acids—were obtained. During this period, a large number of similar compounds have been synthesised and investigated, as can be seen from the extensive monograph, review, periodical, and patent literature. Particular attention has been devoted to the study of the complex-forming capacity and practical applications of complexones. The problems of the synthesis and methods for the preparation of polyaminopolyacetic acids are dealt with in a number of reviews[11–14], which are clearly obsolete, and there is a short section in a recently published monograph by Dyatlova et al.[15]

The present review deals with methods for the preparation of only the "true" complexones, i.e. compounds containing one or several iminodiacetic acid groups in the molecule.

There are several ways of synthesising complexones, which can be divided into three groups. The methods of the first group are based on the reactions of various mono- or poly-amines with halogenoacetic acids or formaldehyde and cyanides, which may be combined by the term "carboxymethylation reaction". The second group embraces methods for the preparation of complexones in which the starting material is iminodiacetic acid or its esters. The third group comprises procedures for the preparation of complexones by the modification of the structural analogues or derivatives of iminodiacetic acid as well as other less common procedures.

II. THE CARBOXYMETHYLATION REACTION

This method is most widely used in the synthesis of complexones, since it is based on the employment of fairly readily available amines as the starting materials. The method for the synthesis of complexones by treating amines with halogenoacetate esters followed by hydrolysis of the esters [formed] is closely related.

The "indirect" carboxymethylation reaction—cyanomethylation with simultaneous or subsequent hydrolysis of the nitrile groups—has found fairly extensive applications in the synthesis of complexones.

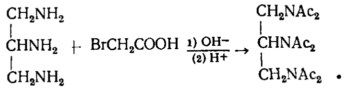
1. Alkylation of Amines by Monohalogenoacetic Acids

The "direct" carboxymethylation reaction is frequently used to prepare complexones under laboratory and industrial conditions. It takes place in accordance with the following mechanism:

$$\mathrm{R{-}NH_2 + HalCH_2COOH \xrightarrow{OH^-} RN(CH_2COO^-)_2 \xrightarrow{H^+} RNAc_2}, \qquad (\mathrm{Ac = CH_2COOH})$$

The reaction consists in the treatment of the amine by a halogenoacetic acid in an alkaline medium. At the end of the reaction, the salt formed is converted into the complexone by acidification.

The carboxymethylating agent most frequently employed is the readily available monochloroacetic acid, which reacts with aliphatic and aromatic mono-, di-, and poly-amines, forming complexones in fairly high yields. In some cases, when the reaction with chloroacetic acid does not proceed, or does not proceed satisfactorily, monobromoacetic acid is used. Thus, when 1,2,3-triaminopropane was treated with chloroacetic acid, the corresponding hexa-acetic acid could not be obtained; the complexone (I) was obtained in a low yield by the reaction of the triamine with bromoacetic acid[16]:

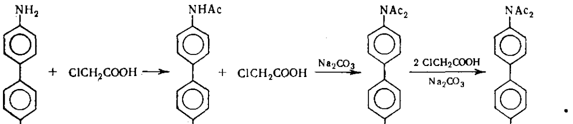


$$\begin{matrix}\mathrm{CH_2NH_2}\\ |\\ \mathrm{CHNH_2}\\ |\\ \mathrm{CH_2NH_2}\end{matrix} + \mathrm{BrCH_2COOH} \xrightarrow[(2)\ \mathrm{H^+}]{1)\ \mathrm{OH^-}} \begin{matrix}\mathrm{CH_2NAc_2}\\ |\\ \mathrm{CHNAc_2}\\ |\\ \mathrm{CH_2NAc_2}\end{matrix}\ .$$

(I)

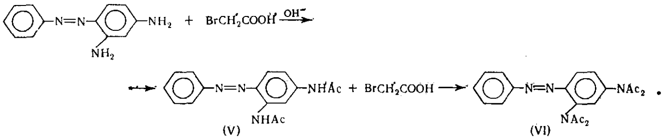
Much higher yields were obtained in the alkylation of 1-phenylethylenediamine and racemic 1,2-diphenylethylenediamine with bromoacetic acid than in the reaction with chloroacetic acid[17]. It follows from the literature data that bromoacetic acid is most frequently used for the carboxymethylation of aromatic amines[18–20]. The use of iodoacetic acid has also been reported[21]. The employment of iodide salts as additives in conjunction with chloroacetic acid, which leads to a more complete and rapid carboxymethylation reaction, has also been described[16,22]. For example, it has been shown[22] that the rate of reaction of aniline with chloroacetic acid increases by approximately 30% in the presence of potassium iodide.

For more complete substitution of the hydrogen atoms of the amino-groups, an excess of halogenoacetic acid, varying in the range 20–100% relative to the stoichiometric amount, is always used. The excess alkylating agent accelerates the reaction, ensures exhaustive carboxymethylation, and "meets the requirement" of the obligatory accompanying side reaction—the hydrolysis of the halogen in the halogenoacetic acid. When a deficiency of halogenoacetic acid is employed, it is possible to isolate products of the incomplete substitution of the amino-groups. Thus when benzidine is heated with one mole of chloroacetic acid in the absence of a condensing agent, benzidinemonoacetic acid (II) is formed[23]. When the reaction is carried out with two moles of the acid in the presence of sodium carbonate, the *NN*-diacetic acid (III) is obtained. On further treatment with chloroacetic acid and Na_2CO_3, the latter yields the tetra-acetic acid (IV):



(II) (III) (IV)

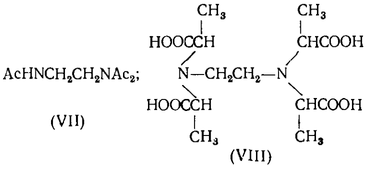
Crysoidinediacetic acid (V) was isolated as an intermediate when crysoidine was treated with bromoacetic acid in molar proportions of 1:6. The corresponding tetra-acetic acid (VI) was obtained by its reaction with bromoacetic acid[25]:



(V) (VI)

On carrying out the reaction of ethylenediamine with chloroacetic acid in molar proportions of 1:3 at a low temperature, Blackmer and Hamm[24] isolated ethylenediaminetriacetic acid (VII) from the reaction mixture in 36% yield and identified it in the form of the cobalt complex. The attempts to isolate this triacetic acid by other procedures proved unsuccessful[25,26]. When a large excess of the halogenoacetic acid is introduced into the carboxymethylation reaction, the isolation and purification of the final product may be hindered.

Apart from halogenoacetic acids, α-halogenopropionic acids may be used to synthesise complexones. Thus ethylenediaminetetra-(α-propionic) acid (VIII) was isolated in 15% yield after the reduction of ethylenediamine and α-chloropropionic acid[27]:



$AcHNCH_2CH_2NAc_2$; (VII)

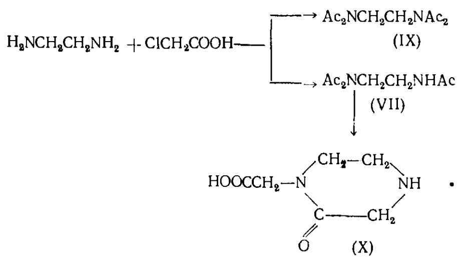
$(HOOCCH(CH_3))_2N-CH_2CH_2-N(CH(CH_3)COOH)_2$ (VIII)

Together with the tetra-acetic acid (VII), di- and tri-substitution products were isolated from the reaction mixture, which indicates steric hindrance to exhaustive alkylation.

The carboxymethylation reaction is always carried out in the presence of bases in order to neutralise the initial halogenoacetic acid, capable of protonating the amine, and to prevent the protonation of the amino-groups during the reaction as a result of the liberation of the proton during alkylation. The protonated amino-group is incapable of reacting with the electrophilic alkylating agent. The use of a neutralising and condensing agent is particularly important in the carboxymethylation of aliphatic amines, since aromatic amines are protonated with much greater difficulty, being much weaker bases. Solutions of sodium hydroxide are frequently used as the condensing agent in the carboxymethylation of aliphatic and aliphatic-aromatic amines. The reaction is carried out at a constant pH (10–11) maintained by the gradual addition of alkali. The employment of sodium carbonates in the carboxymethylation of ethylenediamine has been described[28].

Since the reactions of aromatic and heteroaromatic amines with halogenoacetic acids are carried out at lower pH values (8–10), alkali metal carbonates[28-30] and even magnesium oxide[31] are frequently used together with the alkali. In a few instances, for example in the carboxymethylation of *p*-phenylenediamine[32], the reaction is carried out in the absence of a condensing agent.

As a rule, the alkylation with a halogenoacetic acid is performed in an aqueous medium, but, when amines readily soluble in water are to be alkylated, a solvent miscible with water is sometimes added, mainly acetone[33] and alcohol[34-36]. Several examples of the carboxymethylation reaction using aqueous suspensions of amines have been described[37,38]. The temperature and duration of the reaction are as a rule related. The carboxymethylation of aliphatic and aliphatic-aromatic amines proceeds fairly rapidly (3–10 h) at 40–95°C. An increase of temperature promotes a more complete substitution of the nitrogen atoms, but side reactions are intensified at the same time. A decrease of temperature requires an appreciable increase of the reaction time and incomplete substitution products are then detected in the reaction mixture together with the fully carboxymethylated amines. Genik-Sas-Berezowsky and Spinner[39] investigated in detail the reaction of ethylenediamine with chloroacetic acid at room temperature. After allowing the reaction system to stand for 8 days, they isolated a complex mixture of products consisting largely of ethylenediaminetetra-acetic acid (IX) and ethylenediaminetriacetic acid (VII); the latter cyclised during the reaction to the lactam (X):



$H_2NCH_2CH_2NH_2 + ClCH_2COOH \rightarrow Ac_2NCH_2CH_2NAc_2$ (IX)

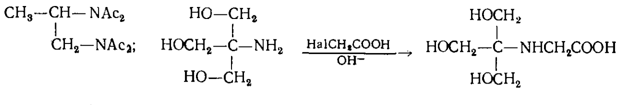
$\rightarrow Ac_2NCH_2CH_2NHAc$ (VII) $\rightarrow$ (X)

On the other hand, it has been shown[40] that, when racemic propylenediamine is heated with chloroacetic acid, the expected tetra-acetic acid (XI) is formed in an insignificant yield, while the reaction carried out in the course of 6 days at 20°C gives an 82% yield of the complexone (XI).

The carboxymethylation of aromatic amines is usually carried out at a higher temperature (of the order of 80–110°C) in order to increase the reaction rate. The duration of the process does not then exceed 4–10 h.

The main reaction, the alkylation of the amines to synthesise complexones by direct carboxymethylation, is to a greater or lesser extent accompanied by side processes, which may have a significant influence on the yield and purity of the final products. The main secondary and competing reaction is the hydrolysis of the halogenoacetic acid in an alkali medium, which reduces the concentrtion of the alkylating agent. This reaction, occurring simultaneously with the main process, is promoted by an increase of temperature and of alkalinity. Together with the hydrolysis of the halogenoacetic acid, the carboxymethylation reaction may involve other side processes, for example the formation of incomplete carboxymethylation products. Apart from temperature and the insufficiency of the alkylating agent, the degree of formation of these side products may be influenced by the structural characteristics of the amines, preventing their exhaustive methylation at the amino-group.

In the carboxymethylation of tri(hydroxymethyl)aminomethane (XII) with chloro- and bromo-acetic acids, it was not possible to introduce two acetic acid residues into the amino-group[41] despite the modification of the reaction conditions; only the monocarboxymethylation product, namely tri(hydroxymethyl)sarcosine (XIII), was always isolated from the reaction mixture:

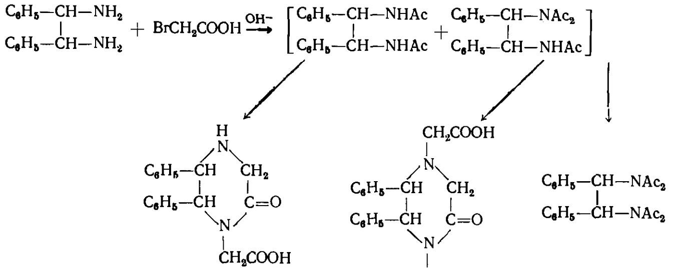


$CH_3-CH(NAc_2)-CH_2-NAc_2$; (XI)

$(HOCH_2)_3C-NH_2 \xrightarrow[OH^-]{HalCH_2COOH} (HOCH_2)_3C-NHCH_2COOH$

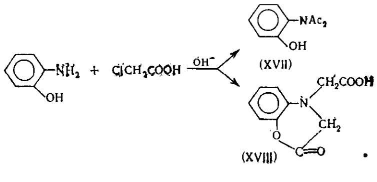
(XII) (XIII)

It has been observed[17] that, in contrast to racemic 1,2-diphenylethylenediamine, the meso-analogue reacts with bromoacetic acid with much difficulty, forming only traces of the tetra-acetic acid (XIV). In this case the main reaction products were the lactams (XV) and (XVI), formed by the cyclisation of the products of the incomplete carboxymethylation of the diamine:



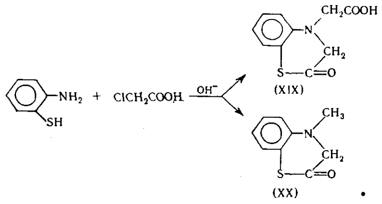
(XV) (XVI) (XIV)

The carboxymethylation reaction may be in many instances complicated by the presence in the molecule of the initial amine of other functional groups or groupings. Thus, when *o*-aminophenol is treated with chloroacetic acid at pH 8–10, the δ-lactone (**XVIII**) is formed together with *o*-hydroxyphenyliminodiacetic acid (**XVII**):[42]



The extent of the latter reaction may be reduced by adding potassium iodide to the reaction mixture[22], which makes it possible to perform the process at a lower pH and reduce thereby the reactivity of the phenolic hydroxyl.

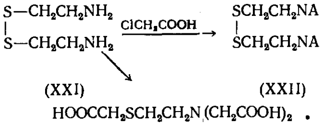
The carboxymethylation of *o*-aminothiophenol proceeds in a more complex manner. On treatment with chloroacetic acid (60°C, pH 8–10), the thiolactone (**XIX**) was isolated from the reaction mixture together with its decarboxylation product (**XX**):[42]



In the amino-β-naphthol series, it was impossible to obtain the corresponding complexone, since naphthoxy-acids are formed under the conditions of "direct" carboxymethylation.

In order to prevent the possible alkylation of the glycolic hydroxyls in 2,3-dihydroxypropylamine, the latter was carboxymethylated at pH < 9 at room temperature[41].

When di(aminoethyl) disulphide (XXI) was carboxymethylated under the conditions leading to the formation of complexones from aliphatic diamines, the expected tetra-acetic acids (XXII) were not isolated[44]. The only reaction product was the triacetic acid (XXIII), the formation of which takes place, according to the authors, as a result of the cleavage of the disulphide linkage in the alkaline medium and alkylation of the nitrogen and sulphur atoms:



(XXI) (XXII)

$HOOCCH_2SCH_2CH_2N(CH_2COOH)_2$.

(XXIII)

This process could not be prevented even by employing oxidising agents. Only when the reaction was carried out in a neutral medium was the previously described[45] tetra-acetic acid (XXII) obtained, but its yield was low.

The mechanism and kinetics of the carboxymethylation reaction have been studied in relation to the interaction of aqueous ammonia with chloro- and bromo-acetic acids[46]. In the first place, it was observed that the rate of reaction of bromoacetic acid with ammonia at 60°C is 26–40 times faster than with the chloroacetic acid. It was found[46] that the reaction proceeds consecutively via an S_N2 mechanism and its maximum rate is reached at pH 10–11. It has been shown that glycine reacts approximately ten times more vigorously with chloroacetic acid than does ammonia:

$$NH_3 \xrightarrow{HalCH_2COOH} H_2NCH_2COOH \xrightarrow{HalCH_2COOH} HN(CH_2COOH)_2 \xrightarrow{HalCH_2COOH} N(CH_2COOH)_3 .$$

Continuing the investigation of the mechanism of the carboxymethylation reaction, Temkina[22] confirmed the consecutive mechanism of the process in relation to methylamine and aniline. She found that the rate-limiting stage of the reaction is the addition of the first carboxymethyl group.

The "direct" carboxymethylation reaction is applicable to a wide variety of amino-compounds. The reaction of chloroacetic acid with ammonia proceeds smoothly and leads to the formation of nitrilotriacetic acid (NAc_3). Under the same conditions, hydrazine leads to hydrazine-*NN*-diacetic acid[30]; semicarbazide-*NN*-diacetic acid ($NH_2CONHNAc_2$) is obtained similarly[30].

A series of *N*-alkyl-derivatives of iminodiacetic acid, from the methyl derivatives to the $C_{15}H_{31}$ analogue, have been synthesised by the "direct" carboxymethylation reaction[35,47].

The preparation of certain derivatives of alkyliminodiacetic acid (XXIV, a – f), containing functional groups in the alkyl chain, by the reaction of the corresponding substituted alkylamines with chloro- or bromo-acetic acid, has been described[48–52].

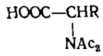
The "direct" carboxymethylation method has been used successfully to synthesise cyclohexyl derivatives (XXV, a and b) [42,53], benzyl derivatives (XXVI, a –g) [50,54–57], and phenylethyl derivatives (XXVII) [50,58,59] of iminodiacetic acid and also to synthesise heterocyclic complexones (XXVIII, a – i) [33,37,60–63] with a single iminodiacetic acid group. These complexones are listed below (together with the appropriate references):

$HOCH_2CH_2NAc_2$

(XXIV a)[48,49]

$HOOCCH_2CH_2NAc_2$

(XXIV b)[50,51]



$$\underset{NAc_2}{HOOC—CHR}$$

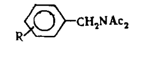
(XXIV) c—R=CH_3
d—R=iso-C_4H_9[50]

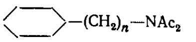
$HO_3SCH_2NAc_2$

(XXIV e)[51,52]

$HO_3SCH_2CH_2NAc_2$

(XXIV f)[51]



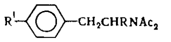


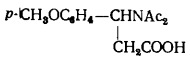
(XXV) a—$n=0$[53]
b—$n=1$[42]

(XXVI) a—$R=H$[55,56]
b—$R=o\text{-}NO_2$[57]
c—$R=n\text{-}NO_2$[57]

$C_6H_5CHRNAc_2$

(XXVI) d—$R=C_6H_5$[54,57]
e—$R=COOH$[50]
f—$R=CH_2COOH$[50]

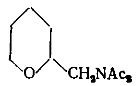




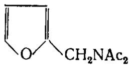
$p\text{-}CH_3OC_6H_4\text{—}\underset{\displaystyle CH_2COOH}{\underset{|}{C}}HNAc_2$

(XXVI g)[50]

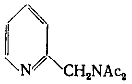
(XXVII) a—$R=H$; $R'=H, OH, OCH_3$[59]
b—$R=COOH$; $R'=H$[50,58]



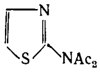
(XXVIII a)[60]



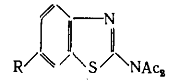
(XXVIII b)[60]



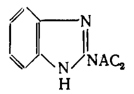
(XXVIII c)[61]



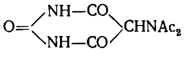
(XXVIII d)[33,42]



(XXVIII) e—$R=H$[61]
f—$R=CH_3$[62]
g—$R=CH_3O$[33]

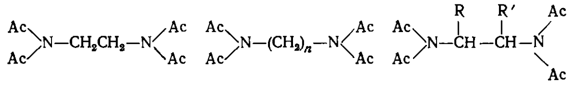


(XXVIII h)[62]



(XXVIII i)[37,63]

A large number of examples of the synthesis of complexones by the direct carboxymethylation of aliphatic amines have been described in the periodical and patent literature. Ethylenediaminetetra-acetic acid (EDTA)[64,65], its homologues with hydrocarbon chain lengths ranging from 3 to 10 (XXIX) [54,66,67], as well as derivatives with methyl [(XI) [40] and (XXX) [68]] and aryl [(XIV) [17] and (XXXI) [69]] substituents in the ethylene chain:



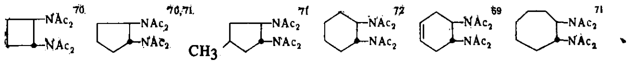
EDTA

(XXIX) $n=3\text{—}10$

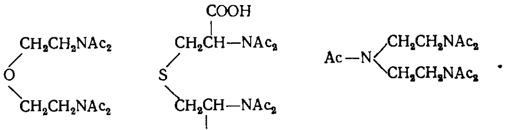
(XXX) $R=R'=CH_3$;

(XXXI) $R=Ph$, $R'=H$.

A series of cyclic analogues of EDTA have been obtained by the condensation of alicyclic 1,2-diamines with chloro- and bromo-acetic acids[69-72]:



The direct carboxymethylation method has found extensive applications in the synthesis of analogues of ethylenediaminetetra-acetic acid containing heteroatoms or functional groups in the hydrocarbon chain. In contrast to di(aminoethyl) disulphide (see above), the carboxymethylation of the corresponding ether to (XXXI) [72] and the sulphide with carboxy-groups to (XXXIII)[74] proceeds normally:

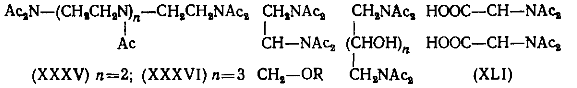


(XXXII)

(XXXIII)

(XXXIV)

The EDTA analogues with amino-groups in the hydrocarbon chain have attracted much attention in view of their high complex-formation capacity. The direct carboxymethylation method has proved extremely convenient for the synthesis of diethylenetriaminepenta-acetic acid (XXXIV) [74]—one of the most effective complexones, which has found applications in engineering, medicine, and agriculture[5]. Its higher homologues triethylenetetraaminehexa-acetic acid (XXXV) and tetraethylenepentaaminehepta-acetic acid (XXXVI) have been synthesised by the same method[75]. *N*-Substituted diethylenetriaminetetra-acetic acids (XXXVII) have been obtained in fairly high yields from the corresponding diamines and chloroacetic acid[76-79]:

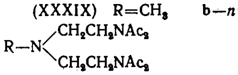


(XXXV) $n=2$; (XXXVI) $n=3$

(XXXVIII) $R=H$
(XXXIX) $R=CH_3$

(XL) a—$n=2$
b—$n=4$

(XLI)

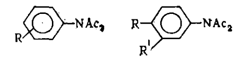


(XXXVII)

$R=C_4H_9$; $C_6H_5CH_2$; C_8H_{17}
$HOCH_2CH_2$; $HOOCCH_2CH_2$

The carboxymethylation of di- and tri-amines containing hydroxy-groups in the hydrocarbon chain takes place smoothly. 2,3-Diamino-1-hydroxypropanetetra-acetic acid (XXXVIII) and 2,3-diamino-1-methoxypropanetetra-acetic acid (XXXIX)[80], racemic 1,4-diamino-2,3-dihydroxybutanetetra-acetic acid and its *meso*-form (XLa) [81-83], D-*manno*-1,6-diamino-1,6-dideoxy-2,3,4,5-tetrahydroxyhexanetetra-acetic acid (XLb) [84,85], and *N*-hydroxyethyldiethylenetriaminetetra-acetic acid (XXXVII, $R = HOCH_2CH_2$) [86] have been obtained by the same method. Side reactions involving the hydroxy-groups were never observed under these conditions. The formation of the EDTA analogue (XLI) containing carboxy-groups at the carbon atoms in the chain has been described[87] and 1,2,3-triaminopropanehexa-acetic acid, mentioned above, has been synthesised by the same method.

A large number of examples of the preparation of aryliminodiacetic acids with various substituents in the benzene ring [compounds (XLII) and (XLIII)] have been described[18,20,42,88-90]. The complexones with the appropriate references are indicated below:



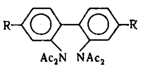
(XLII)

(XLIII)

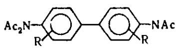
a—$R=H$; *o, m, p*-CH_3; *o, m, p*-CH_3O; *p*-C_2H_5O; *o, p*-Cl[89]
b—$R=$*o, m, p*-OH[88,90]
c—$R=$*o*-$COOH$[88]
d—$R=$*o*-AsO_3H_2[18].

a—$R=COOH$; $R'=OH$[90]
b—$R=CH_3$; $R'=CH_3O$[20]

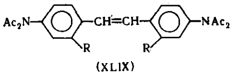
o-, *m*-, and *p*-Phenylenediaminetetra-acetic acids (XLIV) [91]; (XLV, a and b) [23,92,93], and (XLVI, a and b) [21,22,94], a series of diaminobiphenyltetra-acetic acids (XLVII) [34] and (XLVIII) [25,95] and diaminostilbenetetra-acetic acids (XLIX) [38,96], as well as a complexone of the triphenylmethane series (L) [97] have been synthesised by the same method:



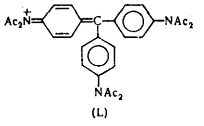
(XLVII)
R = H, CH$_3$, OH, CH$_3$O, NH$_2$



(XLVIII)
R = H, 2-OH, 2-COOH, 2-COOCH$_3$:
2-SO$_3$H, 3-CH$_3$, 3-CH$_3$O, 3-C$_2$H$_5$O

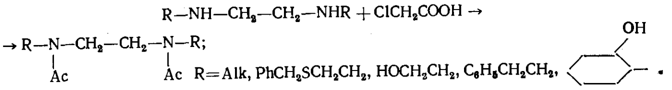


(XLIX)
R = H, SO$_3$H

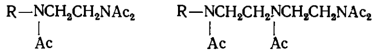


(L)

The carboxymethylation reaction has been used to prepare analogues of ethylenediamine-*NN′*-diacetic acid with various substituents at the nitrogen atom[58,98-100]:



The simultaneous carboxymethylation and arylalkylation or arylation of ethylenediamine, resulting in the formation of EDTA analogues of type (LI), has been described[101]:



$$\underset{\mathrm{Ac}}{\mathrm{R{-}N}}\mathrm{CH_2CH_2NAc_2} \qquad \underset{\mathrm{Ac}}{\mathrm{R{-}N}}\mathrm{CH_2CH_2}\underset{\mathrm{Ac}}{\mathrm{N}}\mathrm{CH_2CH_2NAc_2}$$

(LI) (LII)

$R{=}XC_6H_4$; $XC_6H_4CH_2$; $X{=}H, Cl, CH_3$ $R{=}C_8H_{17}$; $C_{15}H_{21}$; $C_{12}H_{25}$; $C_{14}H_{29}$; $C_{16}H_{33}$. p-ClC_6H_4

Similar compounds have been synthesised also from diethylenetriamine, for example (LII)[102,103].

In many cases halogenocarboxylate esters are used instead of the acids themselves. This makes it possible to carry out the reaction in a non-aqueous medium in the absence of alkalis. The iminodiacetate esters thus obtained are converted into the corresponding complexones by hydrolysis:

$$R{-}NH_2 + XCH_2COOAlk \rightarrow RN(CH_2COOAlk)_2 \rightarrow RNAc_2.$$

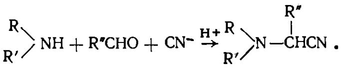
The reaction is carried out as a rule with ethyl monobromoacetate in the absence of a solvent or in alcohol in the presence of potassium carbonate[48]. The esters formed can be purified by distillation. This fact and also the mild reaction conditions make this method very convenient for the synthesis of aliphatic complexones in those cases where an aqueous alkaline medium must be avoided.

2. The Cyanomethylation Reaction

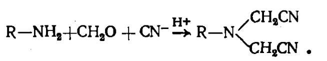
Another method for the carboxymethylation of amines is based on the cyanomethylation reaction. Several versions of this method are used in the synthesis of complexones.

1. Cyanomethylation in an acid medium with formation of the corresponding iminodiacetonitriles and their subsequent conversion into the acids.
2. Cyanomethylation in an alkaline medium with simultaneous hydrolysis of the nitrile groups.
3. Cyanomethylation with the aid of glycolonitrile followed by hydrolysis of the nitrile formed.

Cyanomethylation in an acid medium. This reaction has been known for a long time as the "Strecker reaction"[104] and is widely used in the synthesis of a large variety of aminoacetonitriles[105]. It is based on the reaction of primary or secondary aliphatic amines with aldehydes and hydrocyanic acid. The latter may be replaced by alkali metal cyanides with added acid:



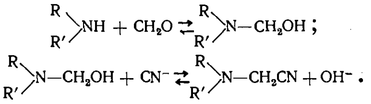
Complexones are synthesised by a specific example of this reaction—the reaction of primary mono-, di-, and poly-amines with formaldehyde and hydrocyanic acid (or its salts in an acid medium) with substitution of both hydrogen atoms in the amino-group by cyanomethyl residues:



The reaction is usually carried out in an aqueous medium at 0–20°C for several hours at pH 1–6.5. Since the use of liquid hydrocyanic acid is relatively inconvenient, sodium or potassium cyanides are usually employed and the added acids are hydrochloric, sulphuric, phosphoric, acetic, or formic acids[106].

The aminonitriles formed in the reaction may be isolated from the reaction mixture and hydrolysed. When water-soluble nitriles are obtained, they are converted into acids without isolation. The hydrolysis of iminodiacetonitriles proceeds most smoothly on heating with alkali or barium hydroxides. Inorganic acids are used for this purpose less frequently.

According to current ideas, the cyanomethylation of amines proceeds via a stage involving the formation of hydroxymethyl derivatives:

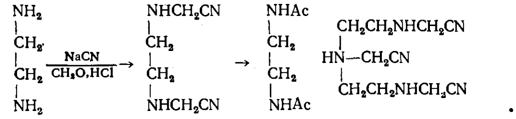


Di(cyanomethyl) derivatives are probably formed in a similar manner.

The introduction of a single cyanomethyl residue into both aliphatic and aromatic primary amines proceeds readily and smoothly. However, the substitution of a second hydrogen atom by the cyanomethyl group is much more difficult, owing to the sharp reduction of the basicity of the monocyanomethylated amino-group[107].

The cyanomethylation reaction is therefore most widely used in the synthesis of aliphatic complexones. However, in this case too the reaction may be stopped at the first substitution stage. The resulting monocyanomethylamines are converted after hydrolysis into complexone analogues—glycine derivatives. In this respect the cyanomethylation reaction has an advantage over direct carboxymethylation, which cannot as a rule yield amine monosubstitution products.

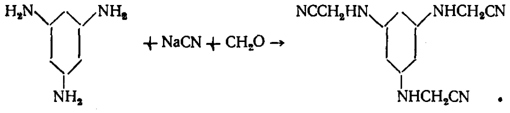
When ethylenediamine is treated with two moles of sodium cyanide and formaldehyde in hydrochloric acid, ethylenediamine-*NN′*-di(acetonitrile) (LIII) is obtained in a high yield and after hydrolysis gives rise to ethylenediamine-*NN′*-diacetic acid (LIV), which is the starting material for the synthesis of complexones[39,108-110]:



(LIII) (LIV) (LV)

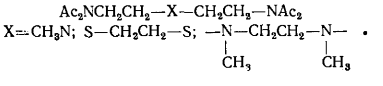
The *NN′N″*-tricyanomethyl derivative (LV) has been synthesised by treating diethylenetriamine with three moles of hydrocyanic acid and formaldehyde[110].

Having treated *cis*, *cis*-1,3,5-triaminocyclohexylamine with sodium cyanide in alcoholic hydrochloric acid, Zompa and Shindler[111] obtained the corresponding tri(aminoacetonitrile) (LVI):



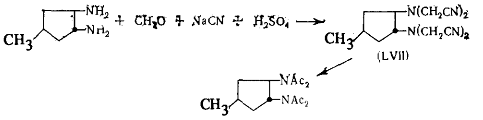
(LVI)

A series of iminodi(acetonitrile) derivatives with aliphatic[45,48] and aliphatic-aromatic[111] substituents have been obtained by the cyanomethylation reaction in an acid medium. Several examples of the synthesis by this method of cyanomethylated di-, and poly-amines, which were converted by hydrolysis into complexones of the type of ethylenediaminetetra-acetic and diethylenetriaminepenta-acetic acids[112-114], including tetra-acetic acids containing a hydroxy-group [compound (XXXVIII)][80] or heteroatoms [(compound (LVII)] in the chain joining the two imino-diacetic acid groups have been described[45]:



$$Ac_2NCH_2CH_2—X—CH_2CH_2—NAc_2$$
$$X{=}CH_3N;\ S—CH_2CH_2—S;\ —\underset{\displaystyle CH_3}{N}—CH_2CH_2—\underset{\displaystyle CH_3}{N}— \ .$$

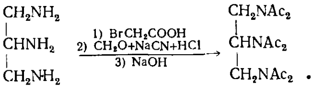
"Acid" cyanomethylation is used in those cases where the synthesis of aliphatic complexones by "direct" carboxymethylation involves difficulties. Thus, when *trans*-1,2-diamino-3-methylcyclopentane was treated with chloroacetic acid, the corresponding tetra-acetic acid could not be isolated[71]. The cyanomethylation of this diamine gave a 32% yield of the tetranitrile (LVII), which was then hydrolysed to *trans*-1,2-diamino-3-methylcyclopentanetetra-acetic acid (LVIII):



(LVII)

(LVIII)

It was already mentioned above that, when 1,2,3-triaminopropane is treated with bromoacetic acid, the corresponding hexa-acetic acid (LIX) is formed in a low yield[16]; the authors succeeded in synthesising this complexone in 84% yield by treating the reaction mixture (after carboxymethylation) with formaldehyde and sodium cyanide in an acid medium and subsequent hydrolysis:



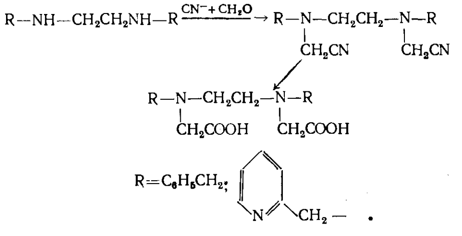
$$\begin{array}{l} CH_2NH_2 \\ | \\ CHNH_2 \\ | \\ CH_2NH_2 \end{array} \xrightarrow[3)\ NaOH]{1)\ BrCH_2COOH \quad 2)\ CH_2O+NaCN+HCl} \begin{array}{l} CH_2NAc_2 \\ | \\ CHNAc_2 \\ | \\ CH_2NAc_2 \end{array} .$$

(LIX)

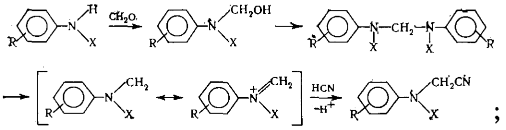
The cyanomethylation reaction in an acid medium has been used to synthesise complexones and their analogues from aliphatic secondary amines. Schwarzenbach et al.[48] synthesised cyanomethyliminodiacetic acid by treating iminodiacetic acid with formaldehyde and sodium hydroxide in hydrochloric acid:

$$HN(CH_2COOH)_2 + NaCN + CH_2O + HCl \rightarrow NCCH_2NAc_2.$$

The synthesis of *NN'*-di(carboxymethyl) derivatives of ethylenediamine by cyanomethylation in an acid medium has been described[115]:



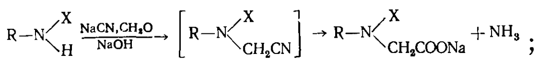
Satisfactory results were obtained in the cyanomethylation of ammonia in an acid medium; this results in the formation of a high yield of tri(cyanomethyl)amine, which is converted into nitrilotriacetic acid by hydrolysis with alkali[116-120]. Being weaker bases, aromatic amines enter into the cyanomethylation reaction with greater difficulty than aliphatic and aliphatic-aromatic amines. The introduction of the second cyanomethyl residue requires the use of glacial acetic acid as the solvent and formaldehyde must be replaced by paraformaldehyde[121,122]. However, this method is suitable only for aniline derivatives without electronegative substituents. Derivatives containing such substituents must be di(cyanomethylated) in the presence of a catalyst—zinc chloride[121]. It is suggested[122] that the cyanomethylation of aromatic amines proceeds in accordance with the following mechanism:



X = H, or CH₂CN .

Under the above conditions, arylaminodiacetonitriles can be obtained in 60–90% yield.

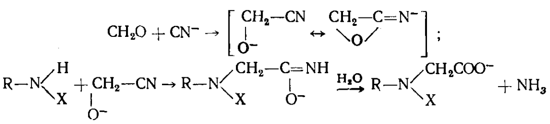
Cyanomethylation in an alkaline medium. The cyanomethylation of amines can be carried out by heating in an alkaline medium[123-130]. Under these conditions, the acetonitriles formed are hydrolysed to the corresponding acids with evolution of ammonia:



$$R—N\begin{smallmatrix} X \\ H \end{smallmatrix} \xrightarrow[NaOH]{NaCN,CH_2O} \left[R—N\begin{smallmatrix} X \\ CH_2CN \end{smallmatrix}\right] \rightarrow R—N\begin{smallmatrix} X \\ CH_2COONa \end{smallmatrix} + NH_3\ ;$$

$X{=}H;$ or $CH_2CN.$

If the ammonia is not removed from the reaction mixture, it is cyanomethylated with formation of nitrilotriacetonitrile and then nitrilotriacetic acid[126,131]. In order to avoid this side reaction, a method was developed in which the cyanomethylating components are introduced periodically with subsequent repeated distillation of ammonia at a reduced pressure during the reaction[124,130,132]. It has been suggested that the cyanomethyl derivatives are not formed in an alkalkine medium, the initial products of the reaction of the cyanide and formaldehyde being glycolonitrile or its salts, the subsequent interaction of which with the amine immediately leads to the formation of the iminodiacetate salt[124-126]:

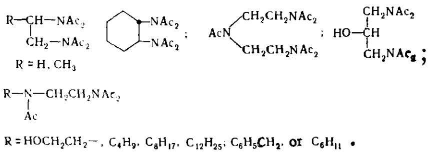


$X{=}H,$ or CH_2CN $\quad X{=}H;$ or CH_2COO^- .

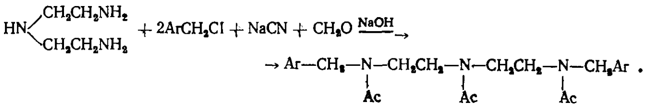
It is suggested that the alkalinity of the medium is necessary for the formation of the glycolonitrile alkoxide ion, which catalyses the cyanomethylation reaction[133].

The yield of polyaminopolycarboxylic acids obtained by this procedure is nearly quantitative when ammonia is rapidly eliminated and the cyanomethylating agents are introduced slowly[134]. As in acid cyanomethylation, in this case it is also possible to carry out the process in a single stage, i.e. one carboxymethyl group may be introduced at each nitrogen atom. It has been found[108,109] that the optimum conditions for this process obtain when the pH of the reaction medium is maintained at approximately 9. Cyanomethylation in an alkaline medium proved to be a convenient procedure for the synthesis of ethylenediamine-*NN*-diacetic acid (LIV), mentioned above[108,109,135]. Its analogues and derivatives can be synthesised similarly[101,108,109,124].

Although the synthesis by the alkaline cyanomethylation method of complexones with a single iminodiacetic acid group, for example nitrilotriacetic acid[131], butyl- and cyclohexyl-iminodiacetic acids[130], and ethyl- and hydroxyethyl-iminodiacetic acids[127], has been described, in the main this method is used to synthesise polyaminopolycarboxylic acids[109,124,130,132,136]. Complexones obtained by this method are indicated below:



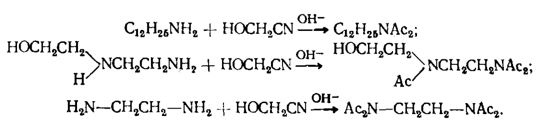
As for direct carboxymethylation, the use of alkaline cyanomethylation simultaneously with arylalkylation of polyamines for the synthesis of complexones with aryl substituents has been described[102,137], for example:



$$HN\begin{matrix}\diagup CH_2CH_2NH_2\\ \diagdown CH_2CH_2NH_2\end{matrix} + 2ArCH_2Cl + NaCN + CH_2O \xrightarrow{NaOH} \to Ar{-}CH_2{-}\underset{\underset{Ac}{|}}{N}{-}CH_2CH_2{-}\underset{\underset{Ac}{|}}{N}{-}CH_2CH_2{-}\underset{\underset{Ac}{|}}{N}{-}CH_2Ar\ .$$

Satisfactory results were obtained when alkaline cyanomethylation was used in the synthesis of aryliminodiacetic acids: *o*-carboxyphenyliminodiacetic acid[127] and certain naphthalene complexones[22,43,76,90,138] have been synthesised in fairly high yields.

A very interesting modification of the cyanomethylation reaction involves treating amines with glycolonitrile[139,140]. The reaction is carried out at pH 11–12 in an aqueous medium heated to 90°C. It has been shown for dodecylamine, ethylenediamine, and hydroxyethylethylenediamine as examples that the corresponding complexones are obtained in nearly quantitative yields under these conditions[139]:



$$C_{12}H_{25}NH_2 + HOCH_2CN \xrightarrow{OH^-} C_{12}H_{25}NAc_2;$$
$$\begin{matrix}HOCH_2CH_2\diagdown\\ H\diagup\end{matrix}NCH_2CH_2NH_2 + HOCH_2CN \xrightarrow{OH^-} \begin{matrix}HOCH_2CH_2\diagdown\\ Ac\diagup\end{matrix}NCH_2CH_2NAc_2;$$
$$H_2N{-}CH_2CH_2{-}NH_2 + HOCH_2CN \xrightarrow{OH^-} Ac_2N{-}CH_2CH_2{-}NAc_2.$$

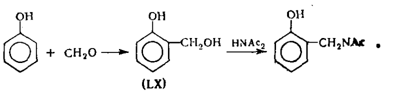
III. THE SYNTHESIS OF COMPLEXONES FROM IMINODIACETIC ACID AND ITS ESTERS

This group of methods combines two procedures for the synthesis of complexones: 1. The reaction of iminodiacetic acid with phenols and formaldehyde (the Mannich reaction). 2. The condensation of iminodiacetic acid and its esters with halogeno-derivatives.

The Mannich Reaction

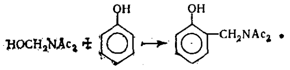
The reaction of iminodiacetic acid with phenols and formaldehyde is a special case of the Mannich reaction[141]. It is usually carried out in acetic acid (pH 2–3) at 5–10°C [87,142,143], but it can also be performed in an alkaline medium at pH ⩽ 10.[87,144] The reactants are usually introduced into the reaction in equimolar amounts[87].

It has been suggested[22] that the first stage of this reaction, carried out in an aqueous medium, is the formation of the phenolic alcohol (LX), which then interacts with iminodiacetic acid, the process being accompanied by the elimination of water:



However, there is no direct evidence for this mechanism and one cannot therefore rule out the possibility that the process can also proceed via a different mechanism:

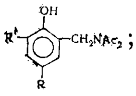
$$CH_2O + HNAc_2 \longrightarrow HOCH_2NAc_2\ ;$$



The problem of the mechanism of the Mannich reaction still continues to be controversial; views have been expressed in the literature concerning the above two mechanisms of this reaction[145,146].

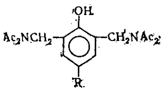
The formation of complexones in both acid and alkaline media is accompanied by side reactions leading to the formation of various admixtures and side products, caused mainly by the oxidation of phenols and the interaction of the latter with formaldehyde, leading to the formation of phenol-formaldehyde oligomers and polymers, methylenebisphenol compounds, phenolic poly(hydroxymethyl) derivatives, etc.

Not only phenol itself[145], but also its methyl and other derivatives[87,142,144,147-149] react with iminodiacetic acid, the methyleneiminodiacetic acid group always entering the *ortho*-position with respect to the hydroxy-group:



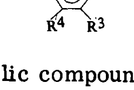
; R = R' = H ;
R = CH₃; R' = H ;
R = NO₂; R' = H ;
R = R' = CH₃ .

Interesting studies on the application of the Mannich reaction in the synthesis of complexones have been carried out by Temkina and coworkers[76,140,142,143,150-152]. They showed that phenol and *p*-cresol can form di(methyliminodiacetic) acid derivatives (LXI) and (LXII)[142,148]. The analogous compound (LXIII) has been obtained from *p*-hydroxybenzenesulphonic acid[153-156]:

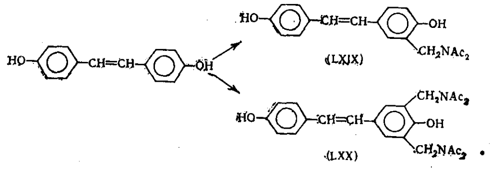


; (LXI) R = H ;
(LXII) R = CH₃ ;
(LXIII) R = SO₃H .

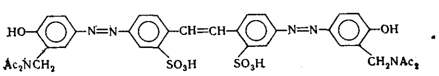
The same workers succeeded in introducing dihydric phenols and even phloroglucinol into the Mannich reaction with iminodiacetic acid[150-152]. It has been shown (Table 1) that the complexones formed under these conditions have the following structure [compounds (LXIV)–(LXVIII)]:



More complex phenolic compounds also undergo the Mannich reaction. Interesting results have been obtained for the reaction of iminodiacetic acid and formaldehyde with dihydroxystilbene[157]. For equimolar reactant ratios, the product is the monosubstituted derivative (LXIX); a second methyleneiminodiacetic acid group enters the same ring compounds (LXX):



The substitution in stilbenediazo-derivatives involves both benzene rings, containing a phenolic hydroxyl, with formation of a symmetric product (LXXI)[158]:



(LXXI)

Table 1.

Compound	R	R1	R2	R3	R4
(LXIV)	$CH_2N(CH_2COOH)_2$	H	OH	H	H
(LXV)	$CH_2N(CH_2COOH)_2$	H	OH	$CH_2N(CH_2COOH)_2$	H
(LXVI)	OH	$CH_2N\begin{matrix}CH_2COONa\\CH_2COOH\end{matrix}$	H	H	H
(LXVII)	$CH_2N(CH_2COOH)_2$	OH	H	H	H
(LXVIII)	OH	$CH_2N(CH_2COOH)_2$	OH	H	H

Complexones have been synthesised by the Mannich reaction from indophenol and its derivatives (LXXII) and (LXXXIII)[159-166] (Table 2):

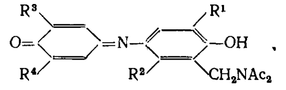
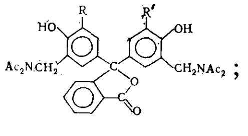


Table 2.

Compound	R^1	R^2	R^3	R^4	Compound	R^1	R^2	R^3	R^4
(LXXII)	H	H	Cl	Cl	(LXXVIII)	C_2H_5	CH_3	Cl	Cl
(LXXIII)	H	H	Br	Br	(LXXIX)	C_2H_5	CH_3	Br	Br
(LXXIV)	CH_3	H	Cl	Cl	(LXXX)	OCH_3	H	Cl	Cl
(LXXV)	CH_3	H	Br	Br	(LXXXI)	OCH_3	H	Br	Br
(LXXVI)	CH_3	CH_3	Cl	Cl	(LXXXII)	H	CH_3	Cl	Cl
(LXXVII)	CH_3	CH_3	Br	Br	(LXXXIII)	H	CH_3	Br	Br

The methods for the introduction of methyleneiminodiacetic acid groups in the synthesis of complexones from phthalein indicators have acquired particular importance. More than 50 compounds of this kind, forming coloured complexes with different metals, have been synthesised by this procedure. Because of this, some of them are used as metalloindicators[1, 167].

The first complexone of this type was 3,3-di-(*NN*-dicarboxymethylaminomethyl)-*o*-cresolphthalein (LXXXIV), synthesised by Schwarzenbach and coworkers, which has been called "phthalein complexone"[144]:

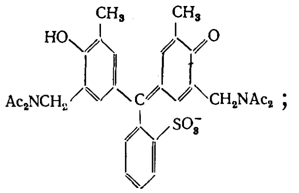


(LXXXIV) $R=CH_3$; $R'=H$;

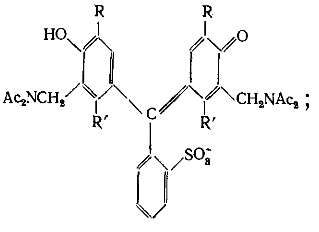
(LXXXV) $R=R'=H$;

(LXXXVI) $R=(CH_3)_2CH$; $R'=CH_3$.

The method for the synthesis of metalloindicators was developed further by Korbl and coworkers[159,160,162,165,168]. They synthesised the phthalein complexone analogues (LXXXV) and (LXXXVI)[168] as well as methyleneiminodiacetic acid derivatives of sulphophthalein (LXXXVII)[169], (LXXXVIII), and (LXXXIX)[159,160,162,165]:



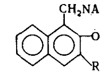
(LXXXVII)



(LXXXVIII) $R=CH_3$; $R'=H$;

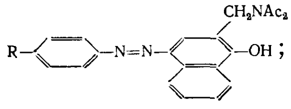
(LXXXIX) $R=(CH_3)_2CH$; $R'=CH_3$.

The aminomethylation reaction can also be used to obtain complexones from condensed phenols. *β*-Naphthol reacts smoothly with iminodiacetic acid and formaldehyde, forming an *α*-substituted derivative of methyleneiminodiacetic acid (XCa)[147, 152]. (3-Carboxy-2-hydroxy-1-naphthyl)methylenediacetic acid (XCb) has been synthesised in a high yield[170]:



(XC) a - R = H; b - R = COOH.

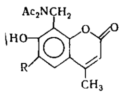
Complexones based on napthalene analogues [compounds (XCI) and (XCII)] have been synthesised similarly to indophenol derivatives[171]:



(XCI) $R=NO_2$;

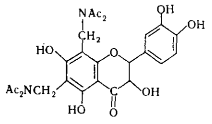
(XCII) $R=SO_3H$.

More complex condensed phenols containing a hydrogen atom in the *o*-position also react with iminodiacetic acid and formaldehyde. The synthesis by this method of fluorescent indicators—iminodiacetic acid derivatives of coumarone [compounds (XCIII) and (XCIV)][172-174], flavone (XCV)[175], and xanthone (XCVI)[172] has been described:

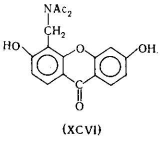


(XCIII) R = H

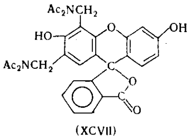
(XCIV) R = OH



(XCV)



(XCVI)



(XCVII)

The complexone (XCVII) has been synthesised from fluorescein[176]. Initially a symmetrical structure was attributed to this compound[176-178], but subsequently it was established that both methyleneiminodiacetic acid groups are in the same benzene ring[153,155].

NN-Di(carboxymethylaminomethyl)anthraquinone derivatives (XCVIII)–(CII)[179] have also been obtained with the aid of the Mannich reaction (Table 3):

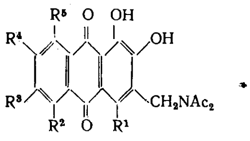
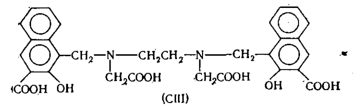


Table 3.

Compound	R^1	R^2	R^3	R^4	R^5
(XCVIII)	H	H	H	H	H
(XCIX)	H	OH	H	H	H
(C)	H	H	OH	H	H
(CI)	H	H	H	OH	H
(CII)	H	OH	H	H	OH

An attempt has been made, with 2-hydroxy-3-naphthoic acid as an example, to use ethylenediamine-*NN'*-diacetic acid as the amino-component in the Mannich reaction[170], but the expected complexone (CIII) was obtained in a yield not exceeding 20%, despite the employment of copper salts as the catalyst:



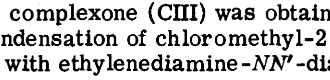
(CIII)

The main reaction product was the corresponding diarylmethane. The complexone (CIII) was obtained in a higher yield by the condensation of chloromethyl-2-hydroxy-3-naphthoic acid with ethylenediamine-*NN'*-diacetic acid[170].

The Reaction of Iminodiacetic Acid and Its Esters with Halogeno-Derivatives

The reaction of iminodiacetic acid with halogeno-derivatives is carried out in an aqueous medium at pH 8.5–9 and a temperature of 40–100°C. Alkali or carbonates may be used as condensing agents. There are potent data[180] concerning the use of this reaction for the synthesis of ethylenediaminetetra-acetic acid.

Satisfactory results were obtained in the condensation of 1,3-dichloro-2-hydroxypropane with iminodiacetic acid (80°C, 5 h) in the presence of alkali; this resulted in the isolation of 1,3-diamino-2-hydroxypropanetetra-acetic acid (CIV) in 52% yield.[181] It was not possible to obtain the tetra-acetic acid by this procedure from *d*- and 1,6-dichloro-1,6-dideoxymannitol[85]:



(CIV)

The synthesis of the tetra-acetic acid (CIV) by treating 2-chloromethyloxiran with iminodiacetic acid has been described recently[182]. Certain analogues of compound (CIV) have been synthesised by this method[182,183].

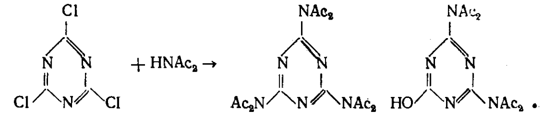
When iminodiacetic acid was treated with chloromethylphosphonic acid (20°C, pH 10–11, 8 days), the complexone (CV) was synthesised[184]:

$$H_2O_3PCH_2NAc_2 \ .$$

(CV)

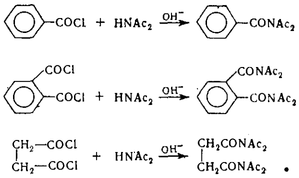
The application of this method to the synthesis of iminodiacetic acid derivatives of triazine proved successful. Thus the corresponding hexa-acetic acid (CVIa) was synthesised by the reaction of cyanuryl chloride with iminodiacetic acid in the presence of an aqueous solution of sodium hydroxide[185].

The tetra-acetic acid (CVIb) was synthesised similarly from 4,6-dichloro-2-hydroxytriazine[185]:



(CVIa) (CVIb)

The condensation of the chlorides of benzoic, succinic, and phthalic acids with iminodiacetic acid in an alkaline medium, resulting in the formation of the corresponding complexones, has been described[186]:



Alkyl sulphates have been used frequently in place of halogeno-derivatives for the alkylation of iminodiacetic acid[187]:

$$(RO)_2SO_2 + HNAc_2 \rightarrow RNAc_2 ;$$
$$R{=}CH_3,\ C_2H_5.$$

The methylation of iminodiacetic acid by the Hess method has also been described[45]:

$$HNAc_2 + CH_2O + HOOCH \rightarrow CH_3NAc_2.$$

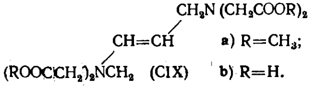
When halogeno-compounds are allowed to react with iminodiacetic acid, there is a difficulty involving the elimination of the initial iminodiacetic acid from the final product. To avoid this, the halogeno-derivatives may be condensed with iminodiacetate esters with subsequent hydrolysis of the ester group in an alkaline medium.

The conditions governing the synthesis of *N*-alkyliminodiacetate esters have been investigated in detail in relation to the reactions of propyl, isopropyl, and allyl bromides with dimethyl iminodiacetate[188]. It has been found that best results are obtained when alcohols isopropyl alcohol and ethylene glycol) are used as solvents and the condensing agent is the iminodiacetate ester itself. Iminodiacetate esters (CVII) are obtained most readily by this method and with a high yield from alkyl or arylalkyl derivatives with a mobile (allyl or benzyl) halogen: dimethyl allyliminodiacetate (CVIIc) was obtained in a yield of about 80%; the yield of tetramethyl *trans*-1,4-diaminobut-2-enetetra-acetate (CIXa) was somewhat lower:

$$R{-}Br + HN(CH_2COOCH_3)_2 \rightarrow RN(CH_2COOCH_3)_2 \rightarrow RNAc_2 ;$$

a) $R{=}n\text{-}C_3H_7$; b) $R{=}iso\text{-}C_3H_7$; (CVII) (CVIII)

c) $R{=}CH_2{=}CH{-}CH_2$



$$(ROOCCH_2)_2NCH_2{-}CH{=}CH{-}CH_2N(CH_2COOR)_2$$

(CIX) a) $R{=}CH_3$; b) $R{=}H$.

The acids (CVIII) and (CIXb) were obtained smoothly from the esters.

Shtacher and Taub[189] described the synthesis by this method of a whole series of aliphatic-aromatic derivatives of iminodiacetic acid (CX). The authors hydrolysed the resulting diesters with sodium hydroxide or lithium hydroxide (in the case of readily soluble acids):

$$R{-}NAc_2$$

(CX)

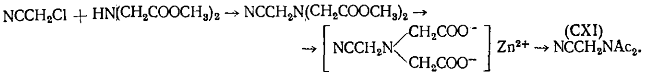
$R = C_6H_5CH_2$; p-$FC_6H_4CH_2$; p-$IC_6H_4CH_2$; 3-OH-4-$BrC_6H_3CH_2$;

$C_6H_5CH_2CH_2$; p-$FC_6H_4COCH_2$; p-$BrC_6H_4COCH_2$; m-$BrC_6H_4COCH_2$;

$C_6H_5OCH_2CH_2$; p-$FC_6H_4OCH_2CH_2$ p-$BrC_6H_4OCH_2CH_2$;

p-$BrC_6H_4NHCOCH_2$; p-$FC_6H_4NHCOCH_2$.

Several alkyl derivatives of iminodiacetic acid with substituents in the hydrocarbon chain have been synthesised by the condensation of halogeno-derivatives with iminodiacetates[48]. Thus dimethyl cyanomethyliminodiacetate (CXI) was obtained in a high yield by the reaction of chloroacetonitrile with dimethyl iminodiacetate without solvent at room temperature. By hydrolysis with zinc perchlorate, it was converted via the zinc salt into cyanomethyliminodiacetic acid (LIX)[48]:



$$NCCH_2Cl + HN(CH_2COOCH_3)_2 \rightarrow NCCH_2N(CH_2COOCH_3)_2 \rightarrow \left[NCCH_2N\begin{smallmatrix} CH_2COO^- \\ CH_2COO^- \end{smallmatrix} \right] Zn^{2+} \rightarrow \underset{}{\overset{(CXI)}{NCCH_2NAc_2}}.$$

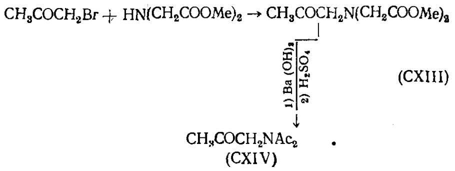
The reaction with chloroacetamide was carried out under the same conditions but with heating to 100°C.

Diethyl 2-nitroethyliminodiacetate (CXII) was synthesised in a quantitative yield by the reaction of 2-chloronitroethane with diethyl iminodiacetate in ethyl acetate at 0°C. However, it could not be hydrolysed, since it proved to be extremely unstable:

$$O_2NCH_2CH_2N(CH_2COOC_2H_5)_2\ .$$

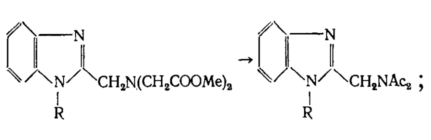
(CXII)

Dimethyl acetonyliminodiacetate (CXIII) was synthesised under the same conditions, but with heating (60–70°C, 4 h), from monobromoacetone and dimethyl iminodiacetate. Without isolation, it was converted into the corresponding iminodiacetic acid (CXVI) in 70% yield[190]:



$$CH_3COCH_2Br + HN(CH_2COOMe)_2 \rightarrow CH_3COCH_2N(CH_2COOMe)_2 \quad (CXIII)$$
$$\xrightarrow{1)\ Ba(OH)_2;\ 2)\ H_2SO_4} \underset{(CXIV)}{CH_3COCH_2NAc_2}\ .$$

The application of this method to the synthesis of heterocyclic derivatives of iminodiacetic acid has been described: 2-chloromethylbenzimidazole and its 1-methyl derivative react with methyl iminodiacetate to give the corresponding diesters (CXV), which are converted by hydrolysis into the complexones (CXVI); the overall yield is about 50%[191]:



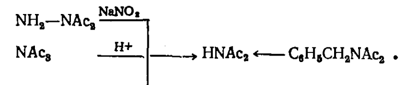
(CXV) (CXVI)

R=H, CH_3.

IV. OTHER METHODS FOR SYNTHESISING COMPLEXONES

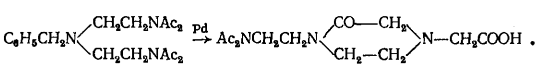
There exist several specific methods for the synthesis of complexones. They include, for example, reactions whereby the molecules of iminodiacetic acid derivatives are modified. Thus the most convenient method for the synthesis of iminodiacetic acid, which is used in industry, involves the cleavage of hydrazine-*NN*-diacetic acid under the influence of sodium nitrite[30, 192].

The synthesis of iminodiacetic acid by the acid cleavage of nitrilotriacetic[193, 194] and semicarbazide-*NN*-diacetic[30] acids and by the catalytic debenzylation of benzyliminodiacetic acid[55] has been described:



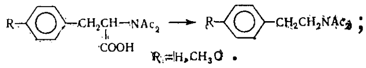
$$NH_2{-}NAc_2 \xrightarrow{NaNO_2};\quad NAc_3 \xrightarrow{H+};\quad NH_2CONHNAc_2 \xrightarrow{H+} \longrightarrow HNAc_2 \longleftarrow C_6H_5CH_2NAc_2\ .$$

Debenzylation has also been used to synthesise diethylenetriaminetetra-acetic acid, which was isolated as the lactam[137]:

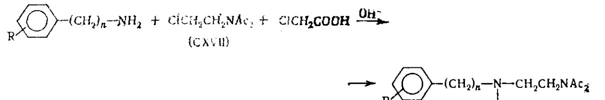


$$C_6H_5CH_2N\begin{smallmatrix} CH_2CH_2NAc_2 \\ CH_2CH_2NAc_2 \end{smallmatrix} \xrightarrow{Pd} Ac_2NCH_2CH_2N\begin{smallmatrix} CO{-}CH_2 \\ CH_2{-}CH_2 \end{smallmatrix}N{-}CH_2COOH\ .$$

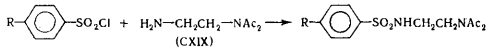
The use of the decarboxylation reaction for the modification of complexones has been described. Thus phenylethyliminodiacetic acid was obtained from phenylalanine[50] and its *p*-methoxy-derivative was synthesised[195]:



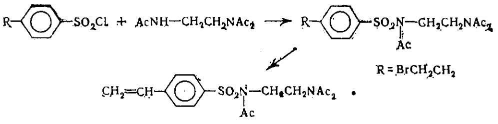
There are several examples of the synthesis of complexones using β-substituted ethyliminodiacetic acids. Thus the interaction of β-chloroethyliminodiacetic acid (CXVII) with arylalkylamines and with chloroacetic acid led to the synthesis of complexones of type (CXVIII).[101] β-Mercaptoethylaminodiacetic acid was synthesised by treating the diacetic acid (CXVII) with sodium hydrogen sulphide[196]:



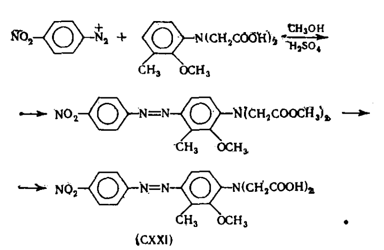
β-Aminoethyliminodiacetic acid (CXIX) was obtained from *N*-acetamidoethyl-*NN*-iminodiacetic acid[197] and was used to synthesise complexones with the sulphonamide group [compounds (CXX)][39]:



Similar reactions have been carried out with ethylenediaminetriacetic acid[39]; the compounds with a bromoethyl substituent thus obtained were converted into vinyl derivatives:

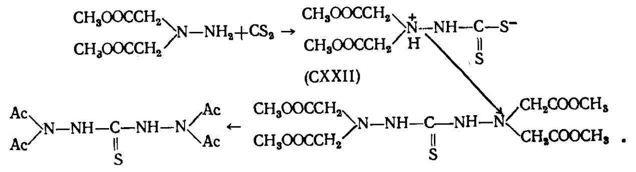


The complexone (CXXI) was synthesised by coupling the *p*-nitrophenyldiazonium cation to 2-methoxy-3-methylphenyliminodiacetic acid[23] in methanol in the presence of sulphuric acid with subsequent hydrolysis of the resulting ester:



(CXXI)

By treating dimethyl hydrazine-*NN*-diacetate with carbon disulphide, Podgornaya[198] obtained a dithiocarbazic acid derivative (CXXII), which yielded thiocarbohydrazide-tetra-acetic acid (CXXIII) after dimerisation in alcohol and hydrolysis:



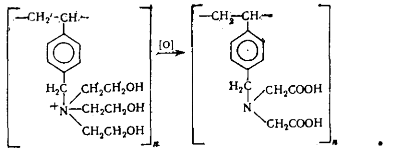
CXXIII

In addition, several examples of the synthesis of complexones by the conversion of *N*-di(hydroxyethyl) groups into aminodiacetic acid groups have been described. The oxidation is carried out in the presence of catalysts (for example, cadmium or its oxide)[199] or under the influence of alkali at 200–260°C.[200] Nitrilotriacetic acid, ethylenediaminetetra-acetic acid, and its analogues have been obtained by this method[200,201]:

$$N(CH_2CH_2OH)_3 \xrightarrow{[O]} N(CH_2COOH)_3;$$

$$(HOCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2OH)_2 \xrightarrow{[O]} Ac_2NCH_2CH_2NAc_2 \ .$$

The method has been used to synthesise polymeric complexones of the type of benzyliminodiacetic acid[202]:



Finally, a method has been described for the synthesis of complexones on the basis of the reaction of amines with aminoacids, particularly with glycine[203]:

$$H_2NCH_2CH_2NH_2 + NH_2CH_2COOH \rightarrow Ac_2NCH_2CH_2NAc_2 + NH_3 \ .$$

The reaction is carried out in an aqueous alkaline medium in the absence of air with elimination of the ammonia formed. However, this interesting reaction has only limited applicability.

Consideration of the existing methods for the synthesis of aminopolycarboxylic acids permits the conclusion that the simplest and universal procedure is the carboxymethylation reaction with mono- and poly-amines as the starting materials. Under laboratory conditions, the direct carboxymethylation method is mainly used, i.e. condensation with halogenoacetic acids. In industry, the procedure based on the cyanomethylation of amines in an alkaline medium competes with the above method, being more economical.

However, the carboxymethylation reaction is in many cases unsuitable for the synthesis of complexones with functional groups, since the latter may undergo transformations under the conditions of these processes, which involve heating with aqueous solutions of alkalis or inorganic acids. Furthermore, the method may suffer from limitations due to the low availability of the initial amines. Other methods of synthesis, based on the employment of halogeno-, hydroxy-, and other derivatives as starting materials instead of amines, may be more successful under these conditions.

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The Polarity and Strength of the Intermolecular Hydrogen Bond

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The results of studies on the dipole moments and the thermodynamics of the formation of complexes with an intermolecular hydrogen bond are reviewed and the nature of the relation between the energies and lengths of intermolecular hydrogen bonds is examined. The enthalpy-entropy relations for the formation of hydrogen-bonded complexes and the linear correlation between the energy of charge transfer and the hydrogen bond energy are analysed and validated. The theoretical and experimental results of the study of hydrogen-bonded complexes are examined from the standpoint of the donor-acceptor nature of hydrogen bonds.

The bibliography includes 240 references.

CONTENTS

I. INTRODUCTION

Numerous studies have been made on hydrogen bonds. The interest in this common type of coordination interaction can be accounted for by its exceptionally important role in many physical, chemical, and biological processes. A number of books[1-6], general reviews[7,8], as well as reviews on specific aspects of the hydrogen bond (theory[9-16], infrared and ultraviolet spectroscopy[17,18], NMR[19-25], and reactivity[26]) have been written. There exists an appreciable gap in the survey of results of studies on the polar properties of hydrogen bonds and in this field there exists only a short and extremely limited review[27].

Nevertheless the dipole moment is one of the most important characteristics of the molecular complex, since it carries information about the nature of the redistribution of electron density and complex formation. This parameter assumes particular importance when hydrogen-bonded complexes are examined from the standpoint of the donor-acceptor interaction, since it makes it possible to assess the role of charge-transfer forces in the stabilisation of hydrogen-bonded complexes.

In the present review, an attempt is made to survey the results of studies on the polar properties of intermolecular hydrogen-bonds, to examine the question of the type of correlation between the polarity and energy of hydrogen bonds, and to discover the common features and differences in the properties of hydrogen-bonded complexes and the usual complexes of the donor-acceptor type (EDA complexes). Mainly studies concerned with hydrogen-bonded complexes formed by neutral molecules A-H and B are dealt with in the review. Furthermore, the results which make it possible to determine fairly reliably the parameters characterising intermolecular hydrogen bonds are given preferential consideration.

It is usual to refer to the components of the (A-H)-B system as acid-base, or proton donor-proton acceptor, or electron acceptor-electron donor respectively. In the main, we shall use the terminology electron donor (B) and electron acceptor (A-H).

II. THE NATURE OF THE HYDROGEN BOND

The theoretical aspect of the hydrogen bond has been examined in detail in the monographs and reviews mentioned above and will not be discussed here. We shall only point out that a characteristic feature of research in this field is a consistent increase in the number and sophistication of studies devoted to both semi-empirical and, particularly, non-empirical (*ab initio*) quantum-mechanical calculations on systems with hydrogen bonds. The latter is to a large extent due to the development of methods for calculations on multielectron systems and to the improvement of computational techniques.

The results of calculations of electron density redistribution and molecular orbital populations on formation of hydrogen bonds are the most important from the standpoint of the understanding of the nature of the hydrogen bond. Despite the wide variety of systems for which calculations have been made, general trends can be recognised[10-12]. When a hydrogen bond is formed, electron density shifts from the donor molecule B to the acceptor molecule A-H. This type of electron density redistribution has been observed also on formation of the usual donor-acceptor bond[28]. This factor justifies the consideration of hydrogen-bonded complexes as complexes of the donor-acceptor type. The magnitude of the transferred charge differs in different systems. For example, it amounts to only 0.0064*e* for the water dimer[29] and to 0.04*e* and 0.07*e* for the more stable complexes[30] $HOH.NH_3$ and $FOH.NH_3$. Here the decrease of electron density at the electron donor atom causes a charge redistribution in the entire molecule B. The greatest increase of electron density is observed in the region of the atom X of the electron acceptor molecule A-X-H.[31-36]

In the solution of the problem of intermolecular interaction, the question of the forces leading to the formation of complexes is extremely important. There have been numerous studies designed to obtain quantitative estimates of the contributions of Coulombic attraction, exchange repulsion, inductive and dispersion interactions, and the stabilisation energy of relatively weak hydrogen bonds[9,11]. Using perturbation theory, Murrell and coworkers[37,38] developed a method which can take into account not only the electrostatic interactions but also the effects of the overlapping of the interacting orbitals of the donor and acceptor molecules. This procedure makes it possible to trace the trend in the changes of individual contributions with increasing strength of the interaction. It has been shown that the role of the inductive and exchange system energies is not great: the main contribution to the energy of hydrogen bonds comes from the Coulombic interaction. The charge-transfer energy is low when the overlap integral S of the interacting orbitals is less than 0.1, but increases rapidly with increase of S.[38] Consequently the contribution of the charge-transfer energy is low for weak hydrogen bonds, becoming more important for moderately strong and strong hydrogen bonds. This hypothesis is consistent with the results from the analysis of the contribution of different forces to the stabilisation energy of the usual complexes of the donor–acceptor type.

The contributions of the polarisation interaction to the dipole moment (μ_C, D) and to the energy of formation (ΔH, kcal mole^{-1}) of a number of charge-transfer complexes are given below:

Complex	μ_C	$-\Delta H$ (calc.)	μ_C	$-\Delta H$ (expt.)
HMB*-chloranil (Ref.39)	0.5—0.9	2.2—2.4	1.0	5.4
HMB*-trinitrobenzene (Ref.39)	1.1—1.5	2.6—3.0	0.87	4.7
$I_2.NH_3$ (Ref.40)	0.91—1.96	0.34—1.68	6.4	4.8
$I_2.N(CH_3)_3$ (Ref.40)	0.30—0.57	0.04—0.13	6.0	10.2

† Hexamethylbenzene.

Comparison of the calculated and experimental values shows that the role of polarisation interaction is considerable in comparatively weakly bonded complexes, the contribution of electrostatic forces being comparable to the contribution of charge-transfer forces. In stronger complexes, the charge-transfer forces predominate over the classical intermolecular interaction forces.

A similar situation probably obtains also for hydrogen-bonded complexes. The hypothesis of a large contribution of charge-transfer forces to the stabilisation energy of hydrogen bonds and of the possibility of considering hydrogen-bonded complexes from the common standpoints of the donor–acceptor interaction and of Mulliken's theory of charge-transfer complexes[41,42] has been frequently put forward[43-48]. In recent years this concept has been increasingly accepted and confirmed experimentally[47,48].

Whereas Mulliken did not classify hydrogen-bonded complexes as electron–donor–acceptor complexes at the time of the creation of his theory[41], in his later studies it is concluded that these two types of interaction are similar and that hydrogen-bonded complexes can be included in the general classification of charge-transfer complexes[42]. The classification is based on the type of interacting orbitals—the highest occupied molecular orbital of the electron donor and the lowest vacant orbital of the acceptor. From this standpoint, compounds of the type A–X–H can be regarded as σ acceptors; charge is transferred from the electron donor to the antibonding orbital of the X–Hσ bond. Hence it follows that the complexes A–H...B can be logically regarded as part of the series of other **EDA** complexes.

The main success of Mulliken's theory is that it explained the appearance in the electronic spectrum after complex formation of a new absorption band, the so called charge-transfer band. The fact that charge-transfer bands have not so far been reliably observed in the spectra of hydrogen-bonded complexes to some extent inhibits the extension of this theory to such complexes[11,12]. Nevertheless, the spectra of the most stable **EDA** complexes of Group **III** metals with different n donors also failed to exhibit charge-transfer bands. Calculations have shown[49,50] that these bands should occur in the region of ultraviolet spectrum which is difficult to investigate experimentally (below 200 nm). Some investigators[46,47,51] suggest with justification that the charge-transfer bands for hydrogen-bonded complexes also occur in the far ultraviolet.

The observed discrepancy between the enthalpies of formation or stability constants of the complexes of a given acceptor A–H with a series of donors B and the ionisation potentials on the latter is sometimes quoted as evidence against the possibility of treating hydrogen-bonded complexes as charge-transfer complexes[11]. It is noteworthy that such a discrepancy is frequently observed also for typical **EDA** complexes[28]. Although the ionisation potential is an important characteristic of the donor molecule, it is not the only quantity which determines the relative stabilities of the complexes. The conditions governing the overlapping of the interacting donor and acceptor molecule orbitals are very important in the formation of an intermolecular bond. This can be seen, for example, from a comparison of the corresponding parameters of the hydrogen-bonded complexes and iodine complexes. The ionisation potentials I (eV) of the analogous amines, phosphines, sulphides, and ethers, the overlap integrals S between the orbital of the corresponding heteroatom (indicated in brackets) and the 5p orbital of iodine or the 1s orbital of the hydrogen atom, and the enthalpies of formation ΔH (kcal mole^{-1}) of the corresponding complexes of iodine (**I₂**) and p-chloro-phenol (**OH**) are listed below:

	$(C_2H_5)_3N$	$(C_2H_5)_3P$	$(C_2H_5)_2S$	$(C_2H_5)_2O$
I[52]	7.58	7.86	8.43	9.55
S (I_2)[28]	0.29 ($2sp^3$)	—	0.23 ($3p$)	0.14 ($2sp^2$)
$-\Delta H$ (I_2)[28]	11.4	—	8.5	4.2
S (O—H)[28]	0.48 ($2sp^3$)	0.37	0.36 ($3p$)	0.43 ($2sp^2$)
$-\Delta H$ (O—H)[53,56]	9.9	8.0*	5.0	6.3

* Data for $(C_4H_9)_3P$.

The overlap integrals of the orbitals involved in the formation of the intermolecular bonds in iodine complexes decrease in the sequence amine > sulphide > ether. The ionisation potentials of these compounds increase in the same sequence. Consequently both parameters, the ionisation potential of the donor and the overlap integral of the interacting orbitals, are responsible for the observed sequence of decreasing enthalpies of formation of the corresponding iodine complexes: amines > sulphides > ethers. Similar relations between I, S, and ΔH have been observed also for hydrogen-bonded complexes in the amine–phosphine–sulphide series. Differences have been observed in oxygen compounds. The ionisation potentials of ethers are much higher than those of sulphides and yet the former give rise to much more stable complexes. This discrepancy can be accounted for by the more effective conditions for the overlapping of the interacting orbitals in the O–H...O (S = 0.42–0.43) linkages[28] than in the O–H...O (S = 0.36)[28] linkages.

From the theoretical standpoint, the increment in the dipole moment $\Delta\mu$ on complex formation is the most interesting property of donor–acceptor complexes. In terms of the approximation of the vector additivity method, $\Delta\mu$ is determined as the vector difference between the dipole moment of the complex μ_C and the dipole moments of the components $\mu_{A\text{-}H}$ and μ_B. $\Delta\mu$ is directly related to the charge transferred from the electron donor molecule to the electron acceptor molecule. The determination of the nature of the relation between the magnitude of the transferred charge and the energy of the donor–acceptor bond is of fundamental importance. Comparison of the theoretical and experimental relations may serve as a criterion of the validity of the hypothesis concerning the significant role of charge transfer in the stabilisation of intermolecular bonds.

A linear relation between the degrees of charge transfer and the enthalpies of formation of the complexes has been established on the basis of extensive experimental data embracing a wide variety of complexes of the donor–acceptor type, the enthalpies of formation of which varied from zero to 20 kcal mole^{-1}.[49] The equation of the straight line is

$$-\Delta H = 35.3\,\frac{\Delta\mu}{e\,r_{\mathrm{DA}}}\,, \tag{1}$$

where ΔH, $\Delta\mu$, and r_{DA} are respectively the heat of formation, the dipole moment increment, and the length of the donor–acceptor bond and e is the electronic charge. A similar linear relation between ΔH and $\Delta\mu$ has been established also for various hydrogen-bonded complexes, the energies of which were between 4 and 26 kcal mole^{-1}.[47,48]

Using the relation between the intensity of the stretching vibration band of A–H in the infrared spectrum of the hydrogen-bonded complex, the energy of formation of the hydrogen bond, and the dipole moment increment on complex formation, Iogansen[57] also concluded that there is a linear relation between ΔH and $\Delta\mu$.

The linear relation between ΔH^0 and $\Delta\mu/er_{\mathrm{DA}}$ follows from Mulliken's theory of charge-transfer complexes, which has been described in fair detail in a number of monographs[28,42,58–61]. Here we shall only quote the fundamental equations necessary for the determination of the nature of the relation between the most important parameters of the complexes. According to Mulliken[40,41], the wave function of the ground state of a molecular complex DA can be formulated to a first approximation as the sum of two terms:

$$\psi_N = a\psi_0\,(\mathrm{D},\mathrm{A}) + b\psi_1\,(\mathrm{D}^+ - \mathrm{A}^-). \tag{2}$$

The wave function ψ_0 refers to the state of the system without bonding. The interaction between the donor D and the acceptor A takes place via the classical electrostatic forces. The function ψ_1 refers to the state in which the electron has been transferred from the donor to the acceptor. The coefficients a and b characterise the contribution of the structure with charge transfer to the ground state of the complex.

The wave function of the complex in the excited state is

$$\psi_E = a^*\psi_1\,(\mathrm{D}^+ - \mathrm{A}^-) - b^*\psi_0\,(\mathrm{D},\mathrm{A}). \tag{3}$$

An approximate solution of the Schrödinger equation yields the following expressions for the energies of the ground and excited states of the complex (E_{N} and E_{E}) respectively and for the coefficient ratios b/a and b^*/a^*:

$$E_N = E_0 - \frac{(H_{01} - E_0S_{01})^2}{E_1 - E_0}\,; \tag{4}$$

$$E_E = E_1 - \frac{(H_{01} - E_1S_{01})^2}{E_1 - E_0}\,; \tag{5}$$

$$\frac{b}{a} = -\frac{H_{01} - E_0S_{01}}{E_1 - E_0}\,; \tag{6}$$

$$\frac{b^*}{a^*} = -\frac{H_{01} - E_1S_{01}}{E_1 - E_0}\,, \tag{7}$$

where

$$E_0 = \int \psi_0 H\psi_0 \mathrm{d}\tau;\ H_{01} = \int \psi_0\hat{H}\psi_1\,\mathrm{d}\tau;\ E_1 = \int \psi_1\hat{H}\psi_1\mathrm{d}\tau;\ S_{01} = \int \psi_0\psi_1\mathrm{d}\tau = \\ = 2S/(1+S^2)^{1/2}$$

are the overlap integrals of the wave functions ψ_0 and ψ_1 and their expression in terms of the overlap integral S of the corresponding interacting orbitals.

The equation for the energy of the charge-transfer band $h\nu_{\mathrm{ct}}$ can be obtained from Eqns. (4) and (5):

$$h\nu_{\mathrm{ct}} = E_E - E_N = (E_1 - E_0)\left[1 + \left(\frac{b^*}{a^*}\right)^2 + \left(\frac{b}{a}\right)^2\right]. \tag{8}$$

The dipole moment increment $\Delta\mu$ due to the charge transfer on formation of the donor–acceptor bond can be expressed as follows according to Mulliken's theory:

$$\Delta\mu = \mu_1(b^2 + abS_{01}), \tag{9}$$

where μ_1 is the dipole moment of the structure with complete charge transfer. It is assumed that approximately

$$\mu_1 = e\,r_{\mathrm{DA}}, \tag{10}$$

where r_{DA} is the distance over which the charge is transferred. If the degree of charge-transfer is defined as $\Delta\mu/er_{\mathrm{DA}}$, then, after substituting Eqn. (10) in Eqn. (9), we obtain

$$\frac{\Delta\mu}{er_{\mathrm{DA}}} = b^2 + abS_{01}. \tag{11}$$

The enthalpy of formation of the complex ΔH can be assumed equal to the difference between the energies of the ground state of the complex and the sum of the energies of the initial components ($E_{\mathrm{A}} + E_{\mathrm{D}}$):

$$\Delta H = E_N - (E_{\mathrm{A}} + E_{\mathrm{D}}). \tag{12}$$

This quantity may serve as a measure of the energy of the donor–acceptor bond.

Simultaneous solution of Eqns. (4), (6), (8), (11), and (12) yields Eqn. (13), which relates the fundamental parameters of the complex—the enthalpy of formation ΔH, the dipole moment of the donor–acceptor bond $\Delta\mu$, and the energy of the charge-transfer band $h\nu_{\mathrm{ct}}$:

$$-\Delta H = \frac{h\nu_{\mathrm{ct}}}{\mathrm{A}} \cdot \frac{\Delta\mu}{er_{\mathrm{DA}}} - [E_0 - (E_{\mathrm{A}} + E_{\mathrm{D}})], \tag{13}$$

where

$$A = a^2\left(1 + \frac{a}{b}S_{01}\right)\cdot\left[1 + \left(\frac{b^*}{a^*}\right)^2 + \left(\frac{b}{a}\right)^2\right].$$

For fairly stable complexes, the term $E_0 - (E_{\mathrm{A}} + E_{\mathrm{D}})$, which is a measure of the energy of the interaction between the donor and acceptor molecules via the classical electrostatic forces, may be regarded as small compared with the first term of Eqn. (13). In this case, Eqn. (13) can be written in the form[28,49,61]

$$-\Delta H^0 = \frac{h\nu_{\mathrm{ct}}}{A} \cdot \frac{\Delta\mu}{er_{\mathrm{DA}}}\,. \tag{14}$$

According to Eqns. (13) or (14), the necessary and sufficient condition for a linear relation between the enthalpy of formation of the complex ΔH^0 and the degree of charge transfer $\Delta\mu/er_{\mathrm{DA}}$ is the constancy of the term $h\nu_{\mathrm{ct}}/A$ for different complexes. Calculations have shown[49] that, within the limits of the accuracy of the estimates, this quantity is indeed constant and equal to 1–2 eV, in agreement with the coefficient (1.5 eV) in the experimental Eqn. (1).

We may note that the attempts to establish the nature of the correlation between the strength and polarity of hydrogen bonds have been made frequently. Thus Sutton and coworkers[62,63] compared the dipole moments of hydrogen-bonded complexes with the equilibrium constants K of the complex-formation reactions. However, owing to the linearity of the relation between ΔH and ΔS (as will be demonstrated below), the values of K cannot serve as a sufficiently reliable measure of the energy of the hydrogen bonds. Toyoda[46] attempted to obtain a theoretical description of the relation between ΔH and $\Delta\mu$ on the basis of Mulliken's theory. The following fairly rough approximations were adopted: $a \simeq 1$, $S_{01} = 0$, $\Delta\mu \simeq b^2\mu_1$, $E_0 =$ const., and $H_{01} =$ const.

Assuming that the entropy of complex formation ΔS is constant for different complexes and using the equilibrium constants as a measure of the strength of the hydrogen bonds, Toyoda obtained the relation

$$\lg K \propto \sqrt{\Delta\mu}.$$

However, he correctly remarks in his paper that there are no theoretical grounds for the constancy of H_{01}.

In a recently published series of investigations[64-67], Ratajczak and Orville–Thomas obtained the following expression using the relations from Mulliken's theory and the same approximations as in Toyoda's work:

$$-\Delta H = \frac{H_{01}}{\mu_1^{1/2}}(\Delta\mu)^{1/2} + E_0. \tag{15}$$

On the basis of Eqn. (15), they concluded that there is a linear relation between ΔH and $(\Delta\mu)^{1/2}$. This correlation was tested using extremely limited experimental data[65].

It must be emphasised that Eqns. (13) and (14), indicating a linear relation between $-\Delta H$ and $\Delta\mu/er_{\text{DA}}$, were obtained[49,61] without introducing any approximations additional to those adopted in the derivation of the fundamental equation of Mulliken's theory.

III. HYDROGEN-BONDED COMPLEXES AND PROTON TRANSFER

The hypothesis that the hydrogen-bonded complex is an intermediate in protonation reactions has been gaining increasing recognition at the present time[12]. Proton transfer between the neutral molecules A–H and B via the mechanism

$$\underset{\text{I}}{\text{A—H} + \text{B}} \rightleftarrows \underset{\text{II}}{\text{A—H}\cdots\text{B}} \rightleftarrows \underset{\text{III}}{\text{A}^-\cdots\text{H—B}^+}$$

is believed to be one of the fastest chemical reactions[68].

Not so much the dynamics of the proton transfer process as the question of the positions of the equilibria indicated above is important for the problem discussed in this review. The position of the equilibrium (I) ⇌ (II) determines in many respects the feasibility and accuracy of the estimation of the parameters of the hydrogen-bonded complexes (see below). The equilibrium (II) ⇌ (III) determines the state to which the measured parameters refer. The thermodynamic parameters of the formation of hydrogen-bonded complexes are relatively insensitive to the position of the equilibrium (II) ⇌ (III), since the energetics of the formation of the complex A–H...B and the ion pair A^+...H–B^- in inert solvents are similar[69].

The problem of the origin of the dipole moment of the hydrogen-bonded complex is most controversial. There are two views. According to one, the dipole moment increment on complex formation is caused mainly by the presence in the system of the highly polar protonated form of the complex A^-...H–B^+. The tautomeric equilibrium (II) ⇌ (III) occurs in solution and the experimental dipole moment includes contributions from the dipole moments of the weakly polar hydrogen-bonded complex and the highly polar ion pair. Hence, $\Delta\mu$ reflects either the tautomeric (II) ⇌ (III) equilibrium constant[27,70-72] or the mole fraction of species with proton transfer[73-75].

The dipole moment increment is interpreted in a different way from the standpoint of the electron donor-electron acceptor interaction in systems with hydrogen bonds. According to this concept, the differences between the values of $\Delta\mu$ for different hydrogen-bonded complexes are not caused by the different contents of the protonated form of the complex in solution but are determined by the different degrees of charge transfer from the molecule B to the molecule A–H in the hydrogen-bonded complexes. Consequently, the experimental dipole moment refers to the given hydrogen-bonded complex and the dipole moment increment on complex formation is determined to a first approximation by the magnitude of the transferred charge. The ion pair (III) is regarded as the limiting state of the hydrogen-bonded complex.

The non-linearity of the relation between $\Delta\mu$ and $\Delta\text{p}K_\text{a}$,[27] where $\Delta\text{p}K_\text{a}$ is the difference between the $\text{p}K_\text{a}$ values of the base and acid, is frequently quoted as one of the pieces of evidence in support of the first view. The S shape of the curves relating $\Delta\mu$ to $\Delta\text{p}K_\text{a}$ is then interpreted from the standpoint of the existence of two forms of the complex, (II) and (III), having different polarities[27,72,74,76]. Furthermore, starting from the investigations of Barrow and coworkers[77,78], who detected by infrared spectroscopy two tautomeric forms of the complex in systems formed by mono- and di-chloroacetic acids with pyridine in chloroform, there have been numerous publications in which the observed changes in the infrared spectra on interaction between acids and bases are treated from the standpoint of the formation of either hydrogen-bonded complexes, or protonated forms of the complex, or of both types of species in equilibrium[79-91]. The latter to some extent justified also the treatment of $\Delta\mu$ from the standpoint of the presence of a tautomeric equilibrium in the system. However, these two types of evidence cannot be regarded as sufficiently reliable.

There exist extensive experimental data showing that the $\text{p}K_\text{a}$ values cannot serve as a reliable measure of the electron-donating and electron-accepting properties of molecules and of the strength of hydrogen bonds. The nature of these parameters is very complex and they characterise not only the proton affinity of the molecule but include also the energy and entropy of hydration of the components[92]. Arnett et al.[93-95] failed to observe a general correlation between the enthalpies of formation of hydrogen-bonded complexes of a number of bases with *p*-fluorophenol in carbon tetrachloride, on the one hand, and the heats of protonation of these compounds in strong acids (sulphuric and fluorosulphonic), on the other, having shown thereby that the concepts of basicity in these processes are not identical. At the same time, an excellent correlation between the heats of protonation of bases in chlorosulphonic acid and the $\text{p}K_\text{a}$ values has been demonstrated on the basis of extensive experimental data[95]. The latter is quite natural, since both parameters characterise the formation of solvated ions in the acid–base interaction.

In a study of the interaction of a number of bases with *p*-fluorophenol in carbon tetrachloride and with *p*-fluorobenzenesulphonic acid in methylene chloride by ^{19}F NMR, Taft and coworkers[96,97] showed that the relative basicity scale obtained relative to *p*-fluorophenol (hydrogen-bonded complexes) differs from the basicity scale obtained for *p*-fluorobenzenesulphonic acid (ion pairs). As in the previous case, the chemical shifts and ΔH values for the systems with *p*-fluorobenzenesulphonic acid are satisfactorily correlated with the pK_a values measured in water. The dependence of the basicity scales on the acid properties of the proton donor has been demonstrated by Hadzi et al.[98]

In a chromatographic study of the complexes of HCl and HBr with different bases, Iogansen et al.[99] concluded that the capacity for the formation of a hydrogen bond in terms of energy is completely inconsistent with the strength of the acid as defined by the dissociation constant. A similar conclusion, namely that the strength of the hydrogen bond is not determined by the tendency of the proton to pass from the acid to the base (which is measured by the pK_a value), was reached on the basis of the infrared spectroscopic measurements of $\Delta\nu$ and ΔH for the complexes of HX (X = F, Cl, Br, or I) with different bases[100,101]. A similar situation has been observed for compounds containing SH and OH groups. Mercaptans are stronger acids than alcohols, but, other conditions being equal, the compounds RSH form weaker hydrogen-bonded complexes than the analogous compounds ROH.[102]

Thus it is clear from the foregoing that the correlations of particular parameters of hydrogen-bonded complexes with pK_a and ΔpK_a should be treated with much caution. The linearity of the relations between pK_a and some parameter of hydrogen-bonded complexes may be expected only in those cases where the acid–base interaction leads to the formation of solvated ions. The parameters of hydrogen-bonded complexes measured in inert solvents should not be correlated, in principle, with pK_a. This applies, in particular, to the $\Delta\mu$–ΔpK_a correlation, as stated above. The linearity of the relations between ΔH, $\Delta\nu$, and other parameters of hydrogen-bonded complexes, on the one hand, and ΔpK_a, on the other, which is sometimes observed, refers as a rule to a narrow range of similar complexes. The position of the equilibrium (II) $\rightleftharpoons$ (III), which is sometimes observed, depends to a large extent on the medium.

In a study of the complexes of nitrophenols with aliphatic amines in benzene and in a benzene–cyclohexane mixture by ultraviolet spectroscopy, Vinogradov and coworkers[69,103,104] demonstrated the possibility of converting the hydrogen-bonded complex into a protonated form when a relatively small excess of the amine is added to the solutions. The influence of the solvent on the degree of conversion of the hydrogen-bonded complexes into a protonated form has been observed in systems comprising *p*-nitrophenol and various bases in chlorobenzene[105] and in the *p*-nitrophenol–ethylenediamine system in methanol, ethanol, dioxan, and their mixtures with water[106]. Analogous observations concerning the influence of the solvent on the state of the equilibrium (II) $\rightleftharpoons$ (III) were reached also for carboxylic acid–base systems[107-110]. Benzoic acid reacts with triethylamine in inert solvents (cyclohexane, carbon tetrachloride, and carbon disulphide) to form hydrogen-bonded complexes, while in acetonitrile and chloroform ionisation takes place[107]. The conversion of the protonated form of the complex of trifluoroacetic acid with dimethylaniline into a molecular hydrogen-bonded complex has been observed by ^{1}H NMR when the system was diluted with an inert solvent[109].

The results of studies of the infrared spectra of the H_2O–HCl and NH_3–HCl systems in a nitrogen matrix are instructive[111,112]. In an isolated matrix, the complexes $H_2O.HCl$ and $NH_3.HCl$ are not ion pairs but consist of molecular complexes with strong hydrogen bonds. On the other hand, the presence of ionic forms is characteristic of these systems in a number of solvents. The presence of only the molecular complex in solution without an appreciable contribution of the protonated form has been demonstrated by ^{19}F NMR for complexes of *p*-fluorophenol with a wide variety of bases in carbon tetrachloride[113] and other inert solvents[114]. The conclusion that hydrogen-bonded complexes are formed in binary systems of carboxylic acids and phenols with pyridine was reached on the basis of infrared spectroscopic data[115].

Hydrogen-bonded complexes without the formation of the protonated form have been observed also for the hexafluoropropanol–triethylamine[116] and acetic acid–pyridine[117] systems in benzene and for systems comprising HF and different bases[118]. The study of the infrared spectra of the binary and ternary systems formed by a number of carboxylic acids, including strong acids such as trifluoro- and trichloro-acetic acids, with different bases led to the conclusion that only hydrogen-bonded complexes are formed; proton transfer was not observed[119]. The study of the dielectric relaxation times of the complexes formed by picric acid with tributylamine in benzene[120,121] showed that species of only one type exist in solution. The conductivities of the solutions were low.

Thus one can evidently assume with adequate certainty that, in the studies on systems with hydrogen bonds in inert solvents, we are dealing in the vast majority of cases with only one type of hydrogen-bonded complex, namely complex (II), and not with a mixture of the two forms (II) and (III). The measured parameters ($\Delta\mu_c$, ΔH, ΔS, etc.) then refer to the complex A–H...B and are not the overall characteristics of the hydrogen-bonded complex–ion pair equilibrium system.

IV. THE COMPOSITION AND THERMODYNAMICS OF THE FORMATION OF HYDROGEN-BONDED COMPLEXES

We shall now examine the problem of obtaining the most reliable data characterising the properties of the complex A–H...B. Apart from the X–H bond, which behaves as an electron acceptor on formation of the hydrogen-bonded complex, the A–H molecule frequently contains electron-donating atoms or groups. These are oxygen, sulphur, and nitrogen atoms in alcohols, mercaptans, and primary and secondary amines respectively and the CO, PO, and SO groups in carboxylic, phosphoric, and sulphonic acids and the π-electron systems in aromatic and unsaturated compounds. Such polyfunctionality leads in the majority of cases to the self-association of the A–H molecules. The structure of the associated species $(AH)_n$ and the degree of association n depend on the composition and structure of the A–H molecules and on the conditions under which they exist (the state of aggregation, the concentrations in solutions, and temperature)[122-152].

Carboxylic acids tend to form in solution preferentially cyclic dimers[125-132,150]. The association of alcohols and phenols is more complex. Dimers, trimers, and higher polymers, to which both linear and cyclic structures have been attributed, are observed in solutions of these compounds[23,123,133-146]. The problem of the structure of the associated species formed by alcohols and phenols has been extensively discussed in the literature for a long time, but, nevertheless, it still cannot be regarded as finally solved[23,123,138].

The capacity for self association depends both on the electron-donating and the electron-accepting properties of the A–H molecules. However, in series of compounds A–H with identical structures the introduction of electronegative substituents into the group A leads to a decrease of the capacity of the A–H molecules for self association simultaneously with increase of their electron-accepting capacity. Such a tendency has been observed for alcohols[23], phenols[23,123,139,143], and carboxylic acids[124,128–131]. For example, the enthalpies of formation ΔH_{dim} (kcal mole^{-1}), and the stability constants K_{dim} (litre mole^{-1}) of chloro-substituted acetic acid dimers in carbon tetrachloride decrease with the increase in the number of chlorine atoms in the acid molecule[129]:

	$-\Delta H_{\text{dim}}$	K_{dim}
CH_3COOH	8.4	1400
$CH_2ClCOOH$	7.8	701
$CHCl_2COOH$	6.7	600
CCl_3COOH	5.6	150

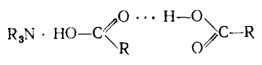
A similar decreased stability of the dimers with increasing degree of halogenation has been observed in a series of substituted fluorophenols[139]:

	$-\Delta H_{\text{dim}}$
2-F—C_6H_4OH	5.2
2,3,5,6-F_4—C_6HOH	3.7
C_6F_5OH	2.9

The decreased stability of the associated species leads to a decrease in the tendency of the A–H molecules towards the formation of higher n-mers $(AH)_n$ with $n > 2$. For example, it has been noted that the self-association of polyfluorophenols proceeds via the monomer ⇌ dimer mechanism, while in solutions of phenols and monofluorophenols, cyclic trimers and tetramers and linear n-mers have been detected[135].

Steric factors also have a significant influence on the capacity of the compounds A–H for self association[132,146]. For example, *ortho*-substituted phenols show less tendency towards self association than their *para-* and *meta*-substituted analogues. The reason for this may be either the formation of intramolecular hydrogen bonds (for example in *o*-nitro and *o*-halogeno-phenols[123,146]) or steric hindrance (for example, the absence of association in 2,6-di-t-butylphenol[146]).

The capacity of the A–H molecules for self-association can lead to the formation, together with the AH...B complexes, also of more complicated complex species having the composition $(AH)_n.B$. The addition of further A–H molecules to AH.B takes place via the same coordination centres as in the self-association of A–H. However, charge transfer from the B molecule to the A–H molecule increases the electron-donating capacity of the latter and the AH...AH linkage is stronger than in the self-associated species[48,53]. For example, the energy of the C=O...H–O hydrogen bond in 2 : 1 complexes of carboxylic acids and amines,



is greater than in the initial acid dimers, the strengthening of this bond being greater the higher the enthalpy of formation of the corresponding complex[48]. The latter is probably associated with the increase of the electron-donating properties of the carbonyl oxygen as a result of charge transfer on formation of the O–H...N linkage.

In view of the self-association of A–H molecules and the possibility of the formation of the complexes $(AH)_n...B$, the interaction in systems with intermolecular hydrogen bonds can be treated as a multistage process:

$$\begin{array}{ll}
AH + AH \rightleftarrows (AH)_2\,; & AH + B \rightleftarrows AH \cdot B\,; \\
(AH)_2 + AH \rightleftarrows (AH)_3\,; & AH \cdot B + AH \rightleftarrows (AH)_2 \cdot B\,; \\
\cdots\cdots\cdots & \cdots\cdots\cdots \\
(AH)_{n-1} + AH \rightleftarrows (AH)_n\,; & (AH)_{n-1} \cdot B + AH \rightleftarrows (AH)_n \cdot B.
\end{array}$$

In solution or in the gas phase, where there is a possibility of the dissociation of the complexes into their components, systems of this kind consist of a complicated equilibrium mixture of complexes having different compositions and of the initial components. In a physicochemical study of such systems, it is necessary to determine simultaneously the parameters of all the complexes present in the mixture, together with their stability constants, which requires the use of special methods for the interpretation of the experimental results[28,153]. If only one comparatively stable complex is formed in the system, the graphical and analytical methods for the interpretation of the measurements[28] used in the study of EDA complexes, which are as a rule approximate, can be applied to the determination of parameters of this complex. For weak interactions or multistage processes, these methods are relatively unsuitable and a rigorous solution of the problem becomes possible only with the aid of a computer[28,53,153].

In order to diminish the degree of self-association of A–H and to avoid the formation of the complexes $(AH)_n.B$, one usually carries out experiments in dilute solutions or a large excess of B is employed. However, the superposition of secondary processes by the appropriate formulation of the experiment is virtually never possible. Thus, if the A–H compounds form fairly stable associated species, self-association can be eliminated only at very low concentrations[53,123] (for example, 0.005 M for phenol[123]). Under these conditions, the comparatively weak complexes AH.B can be fully dissociated into their components or can be present in such low amounts that they cannot be detected because of the limited sensitivity of the given physical method. On the other hand, when a large excess of B is used, there is a possibility of complicating effects associated with the solvating action of the medium[53,94].

The experimental results are frequently treated by approximate computational methods, which are suitable only for single-stage complex-formation processes. At the same time, these methods do not involve criteria which would confirm the occurrence in the system of only one postulated equilibrium and do not allow a choice of the concentration conditions in which the superposition of the side process might be neglected[28,53].

The majority of the methods proposed in the literature for the calculation of equilibrium constants and the physical parameters of complexes from physicochemical data obtained in studies on solutions are based on the hypothesis that the solutions are ideal (the activity coefficients of all the components of the complex-formation reaction are unity). However, under real experimental conditions one is not always dealing with ideal solutions[53,94,154–159]. The thermodynamic non-ideality of solutions results, in particular, from the use of solvents with high dielectric constants (nitrobenzene, dichloroethane, etc.) or from the employment of solutions at high concentrations in the experiments. Furthermore, solvents with electron-donating or electron-accepting properties, such as aromatic hydrocarbons, chloroform, methylene chloride, etc. can enter into specific interactions with the components of the test system. The equilibrium constants determined under such conditions are apparent and do not represent the true values[28].

An enormous amount of data has now accumulated on the thermodynamics of the formation of complexes with intermolecular hydrogen bonds. Most of the literature results have been obtained from the temperature variation of the equilibrium constants using a spectroscopic method (ultraviolet, infrared, Raman, and NMR). The standard free energies ΔG^0, enthalpies ΔH^0, and entropies ΔS^0 are determined from the relations

$$\Delta G^0 = -RT \ln K = \Delta H^0 - T\Delta S^0, \qquad (16)$$

$$T = 298\ ^\circ\mathrm{K};$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \qquad (17)$$

ΔH^0 and ΔS^0 are usually found by a graphical procedure based on Eqn. (17) from the slope of the linear plot of $\ln K$ against $1/T$ and from the intercept on the ordinate axis. The possible errors in the determination of K, which were discussed above, can lead to a very significant distortion of the values of ΔH^0, ΔS^0, and ΔG^0 determined from the equilibrium constants[28].

Iogansen and coworkers[57] proposed a spectroscopic method for the determination of the enthalpies of formation of hydrogen-bonded complexes from the intensities of the stretching vibration bands of the groups X–H in the complex and in the free molecule A–H and not on the basis of the equilibrium constants.

It is noteworthy that an additional source of errors in the determination of thermodynamic parameters by spectroscopic methods may be the overlapping of the absorption bands of the initial components and the complexes and also the possible temperature variation of the molar extinction coefficients[8].

Methods for the estimation of the thermodynamic parameters of hydrogen-bonded complexes on the basis of parametric equations have been proposed in a number of studies[6,56,160–163]. For example, Drago et al.[56] proposed a four-parameter equation:

$$-\Delta H^0 = E_\mathrm{D}E_\mathrm{A} + C_\mathrm{D}C_\mathrm{A}. \qquad (18)$$

The parameters E_D, E_A, C_D, and C_A characterise the electrostatic and covalent properties of the donor and acceptor respectively. The reliability of such parametric methods depends on the accuracy of the estimation of the parameters in the corresponding equations.

The most reliable thermodynamic data for complex-formation reactions can be obtained from direct calorimetric measurements[8,28]. However, here too the accuracy of the determination of the parameters depends to a large extent on the method of mathematical treatment of the results and on the inertness of the medium[28,53]. The Table presents what we believe to be the most reliable thermodynamic parameters (ΔH^0 and ΔS^0) for the complex-formation reactions AH + B $\rightleftharpoons$ AH.B. It includes data obtained in the most inert solvents: hexane, cyclohexane, octane, and carbon tetrachloride, and only in a few instances in benzene, toluene, etc. Preference has been given to calorimetric data. Complexes with enthalpies of formation below 4–5 kcal mole^{-1} have been excluded from consideration because the errors associated with the influence of the medium in such cases are comparable to the parameters being determined. Systems where it is virtually impossible to prevent the superposition of side reactions owing to the strong association of the compounds A–H or owing to the presence of additional coordination centres in the donors B are not considered either.

One of the characteristic features of the thermodynamics of the formation of donor–acceptor complexes of

Thermodynamic parameters and dipole moments of hydrogen-bonded complexes.

No.	Complex	$-\Delta H^0$, kcal mole^{-1}	ΔS^0, e.u.	μ_c, D	$\Delta\mu$, D	Solvent	References
1		3	4	5	6	7	8
1	$CH_3OH \cdot N(C_2H_5)_3$	5.4	16.4	2.6	0.55	CH	167
2	$C_4H_9OH \cdot N(C_2H_5)_3$	4.86	14.3	2.51	0.48	CT, CH	195, 66
3	$C_4H_9OH \cdot NC_5H_5$	3.91	11.4	3.37	0.38	CT, B	196, 222
4	$C_6H_{11}OH \cdot NC_5H_5$	3.98	—	4.23	0.8	B	168
5	$CF_3CH_2OH \cdot N(CH_3)_3$	4.8	4.0	—	—	(gas)	197
6	$(CF_3)_2CHOH \cdot OC(CH_3)OC_2H_5$	5.9	13.0	—	—	CT	154
7	$(CF_3)_2CHOH \cdot OC(CH_3)N(CH_3)_2$	8.22	14.7	—	—	H	154
8	$(CF_3)_2OHCH \cdot OP[N(CH_3)_2]_3$	8.63	10.3	—	—	ODCB	154
9	$C_6H_5OH \cdot O(CH_2)_4$	6.06	15.0	3.20	0.69	CT, CH	198, 167
10	$C_6H_5OH \cdot O(CH_2)_4O$	6.0	14.7	1.85	0.39	CT, CH	199, 66
11	$C_6H_5OH \cdot OC(CH_5)_2$	6.6	16.4	5.02	1.04	CH, B	199, 223
12	$C_6H_5OH \cdot OC(CH_3)C_2H_5$	5.34	12.9	4.42	0.51	CT, B	200, 223
13	$C_6H_5OH \cdot OC(CH_2)_5$	5.1	11.4	—	—	CT	201
14	$C_6H_5OH \cdot OC(CH_3)N(CH_3)_2$	7.36	15.0	—	—	CT	202
15	$C_6H_5OH \cdot OS(CH_3)_2$	7.21	13.7	—	—	CT	202
16	$C_6H_5OH \cdot OP(OC_4H_9)_3$	6.1	11.1	—	—	CT	203
17	$C_6H_5OH \cdot OP(SC_4H_9)_3$	5.7	9.9	—	—	CT	203
18	$C_6H_5OH \cdot OP(C_4H_9)_3$	8.1	12.1	—	—	CT	203
19	$C_6H_5OH \cdot OP[N(CH_3)_2]_3$	9.0	15.1	—	—	CT	203
20	$C_6H_5OH \cdot N(C_2H_5)_3$	8.3	19.4	3.01	1.04	CT, CH	204, 66
21	$C_6H_5OH \cdot NC_5H_5$	8.0	18.1	4.30	0.94	CH, HP	199, 66
22	$C_6H_5OH \cdot 2,6\text{-}(CH_3)_2C_5H_3N$	7.8	15.2	—	0.70	CT	205, 74
23	$C_6H_5OH \cdot 2,4,6\text{-}(CH_3)_3C_5H_2N$	7.5	15.7	4.26	0.78	CT	206, 74
24	$4\text{-}CH_3C_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	5.7	10.4	—	—	CT	207
25	$4\text{-}CH_3C_6H_4OH \cdot NC_5H_5$	6.02	13.0	3.84	0.34	CT	196, 74
26	$3\text{-}CH_3C_6H_4OH \cdot NC_5H_5$	6.15	13.4	4.46	1.02	CT, B	196, 168
27	$4\text{-}C_4H_9C_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	8.1	16.0	—	—	CH	208
28	4-tert-$C_4H_9C_6H_4OH \cdot O(CH_2)_4$	5.6	12.4	—	—	CH	209
29	$3,4\text{-}(CH_3)_2C_6H_3OH \cdot N(C_2H_5)_3$	7.2	16.6	3.80	1.7	O	53, 47
30	$3,4\text{-}(CH_3)_2C_4H_3OH \cdot NC_5H_5$	7.2	17.0	4.60	1.16	O	53, 47
31	$2,6\text{-}(CH_3)_2C_6H_3OH \cdot N(C_2H_5)_3$	5.4	14.5	3.12	0.95	O, B	53, 47
32	$2,6\text{-}(CH_3)_2C_6H_3OH \cdot NC_5H_5$	6.6	17.2	4.5**	0.95**	O	53, 47
33	$3\text{-}CF_3C_6H_4OH \cdot S(CH_3)_2$	5.4	15.2	—	—	CH	56
34	$3\text{-}CF_3C_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	7.3	11.3	—	—	CH	160
35	$3\text{-}CF_3C_6H_4OH \cdot OC(CH_3)OC_2H_5$	6.8	15.3	—	—	CH	160
36	$3\text{-}CF_3C_6H_4OH \cdot OC(CH_2)_5$	7.4	16.4	—	—	CH	160
37	$3\text{-}CF_3C_6H_4OH \cdot NC_5H_5$	8.5	16.6	—	—	CH	202
38	$4\text{-}FC_6H_4CH \cdot O(C_2H_5)_2$	5.6	14.2	—	—	CT	94, 95
39	$4\text{-}FC_6H_4OH \cdot O(CH_2)_4$	5.7	13.1	—	—	CT	202
40	$4\text{-}FC_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	7.44	13.9	—	—	CT	94, 202
41	$4\text{-}FC_6H_4OH \cdot OS(CH_3)_2$	6.6	10.9	—	—	CT	202
42	$4\text{-}FC_6H_4OH \cdot OS(C_4H_9)_2$	6.3	11.3	—	—	CT	94
43	$4\text{-}FC_6H_4OH \cdot ON(CH_3)_3$	8.8	13.3	—	—	CT	94
44	$4\text{-}FC_6H_4OH \cdot ONC_5H_5$	7.5	12.6	—	—	CT	94
45	$4\text{-}FC_6H_4OH.OP(CH_3)_3$	7.7	10.1	—	—	CT	94
46	$4\text{-}FC_6H_4OH \cdot OP(OC_2H_5)_3$	6.5	9.4	—	—	CT	94
47	$4\text{-}FC_6H_4OH \cdot OP[N(CH_3)_2]_3$	8.0	10.6	—	—	CT	202
48	$4\text{-}FC_6H_4OH \cdot N(C_2H_5)_3$	8.92	21.0	—	—	CT	160, 202
49	$4\text{-}ClC_6H_4OH \cdot O(CH_2)_4$	5.8	12.8	—	—	CT	15
50	$4\text{-}ClC_6H_4OH \cdot OC(CH_3)_2$	4.95	10.3	—	—	CT	210
51	$4\text{-}ClC_6H_4OH \cdot OS(CH_3)_2$	6.7	10.9	—	—	CT	211
52	$4\text{-}ClC_6H_4OH \cdot N(CH_3)_3$	7.4	13.0	4.30	1.4	CH	62
53	$4\text{-}ClC_6H_4OH \cdot N(C_2H_5)_3$	9.9	22.4	4.60	1.75	O	53, 47
54	$4\text{-}ClC_6H_4OH \cdot NC_5H_5$	9.4	20.2	5.07	0.83*	O	53, 47
55	$3\text{-}ClC_6H_4OH \cdot OC(CH_3)_2$	5.3	11.0	—	—	CT	210
56	$3\text{-}ClC_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	6.9	11.7	—	—	CT	211
57	$3\text{-}ClC_6H_4OH \cdot N(C_2H_5)_3$	7.9	20.9	—	—	T	212
58	$4\text{-}BrC_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	7.0	11.7	—	—	CT	207
59	$4\text{-}BrC_6H_4OH \cdot OS(CH_3)_3$	6.8	10.9	5,09	0.71	CT, B	211, 224
60	$4\text{-}BrC_6H_4OH \cdot N(C_2H_5)_3$	10.0	21.7	5.1**	2.24**	O	53, 47
61	$4\text{-}BrC_6H_4OH \cdot NC_5H_5$	8.0	16.3	5.24	0.98	O	53, 47
62	$4\text{-}IC_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	6.5	10.6	—	—	CT	211
63	$4\text{-}IC_6H_4OH \cdot OS(CH_3)_2$	6.6	10.4	—	—	CT	211
64	$4\text{-}CH_3OC_6H_4OH \cdot N(C_2H_5)_3$	8.4	—	2.87	0.61	CT, B	213, 70
65	$4\text{-}CH_3OC_6H_4OH \cdot NC_5H_5$	6.09	13.3	3.69	0.19	CT, B	196, 70
66	$3,4\text{-}Cl_2C_6H_3OH \cdot OC(CH_3)N(CH_5)_2$	7.2	12.6	—	—	CT	211
67	$3,4\text{-}Cl_2C_6H_3OH \cdot OS(CH_3)_2$	7.4	11.8	—	—	CT	211
68	$3,4\text{-}Cl_2C_6H_3OH \cdot N(C_2H_5)_3$	8.0	19.5	—	—	CT	212
69	$4\text{-}NO_2C_6H_4OH \cdot OC(CH_3)N(CH_3)_2$	8.2	11.8	—	—	CT	207
70	$4\text{-}NO_2C_6H_4OH \cdot N(C_2H_5)_3$	9.7	28.6	7.55	2.68	B	47
71	$4\text{-}NO_2C_6H_4OH \cdot N(C_4H_9)_3$	9.3	19.6	—	—	ODCB	214
72	$4\text{-}NO_2C_6H_4OH \cdot NC_5H_5$	8.4	16.4	7.31	0.96	ODCB	214, 74
73	$3\text{-}NO_2C_6H_4OH \cdot N(C_2H_5)_3$	8.5	21.7	5.32	1.20	T, B	212, 70–72
74	$3,4\text{-}(NO_2)_2C_6H_3OH \cdot N(C_2H_5)_3$	8.1	11.1	—	—	B	69
75	$3,4\text{-}(NO_2)_2C_6H_3OH \cdot N(C_3H_7)_3$	9.2	17.7	—	—	B	69
76	$3,4\text{-}(NO_2)_2C_6H_3OH \cdot N(C_4H_9)_3$	11.0	18.7	—	—	CH	69
77	$C_6H_5COOH \cdot OS(CH_3)_2$	8.8	20.7	—	—	CT	215, 216
78	$C_6H_5COOH \cdot N(C_2H_5)_3$	15.0**	41.3	4.43	3.9	B	48
79	$C_6H_5COOH \cdot N(C_3H_7)_3$	12.9	26.2	4.28	3.8	B	48
80	$CH_3COOH \cdot N(C_2H_5)_3$	11.6	—	3.61	3.5	B	48
81	$CH_3COOH \cdot N(C_3H_7)_3$	11.9	26.5	—	—	B	—
82	$CH_3COOH \cdot N(C_4H_9)_3$	10.0**	19.1	3.80	3.7	B	48
83	$CH_3COOH \cdot NC_5H_5$	7.0	14.5	3.73	2.1	CT, B	217, 225
84	iso-$C_3H_7COOH \cdot OP(CH_3)_3$	12.0	23.4	—	—	CT	218
85	$CH_2ClCOOH \cdot OS(CH_3)_2$	8.65	11.8	—	—	CT	219
86	$CH_2ClCOOH \cdot OS(C_6H_5)_2$	6.5	7.21	—	—	CT	219
87	$CH_2ClCOOH \cdot OS(CH_2C_6H_5)_2$	7.72	9.39	—	—	CT	219
88	$CH_2ClCOOH \cdot OSe(C_6H_5)_2$	11.8	19.3	—	—	CT	219
89	$CH_2ClCOOH \cdot OP(C_8H_{17})_3$	13.4	21.2	—	—	CT	219
90	$CH_2ClCOOH \cdot OP(C_6H_5)_3$	10.2	16.6	—	—	CT	219
91	$CH_2ClCOOH \cdot N(C_2H_5)_3$	16.2**	42.9	6.71	5.5**	B	48
92	$CH_2ClCOOH \cdot NC_5H_5$	10.3	—	4.80	2.3**	B	48
93	$CH_2BrCOOH \cdot N(C_2H_5)_3$	16.9	46.6	6.84	4.7	B	48
94	$CH_2ICOOH \cdot N(C_2H_5)_3$	16.6	45.6	6.66	4.7	B	48
95	$CHCl_2COOH \cdot OS(CH_3)_2$	9.4	12.0	—	—	CT	219
96	$CHCl_2COOH \cdot OS(C_6H_5CH_2)_2$	9.1	11.8	—	—	CT	219
97	$CHCl_2COOH \cdot OS(C_6H_5)_2$	9.9	7.7	—	—	CT	219
98	$CHCl_2COOH \cdot OSe(C_6H_5)_2$	14.2	23.9	—	—	CT	219

Table (Continued)

No.	Complex	$-\Delta H^0$, kcal mole^{-1}	ΔS^0, e.u.	μ_c, D	$\Delta\mu$, D	Solvent	References
1	2	3	4	5	6	7	8
99	$CHCl_2COOH \cdot OP(C_8H_{17})_3$	23.7	54.4	—	—	CT	219
100	$CHCl_2COOH \cdot OP(C_6H_5)_3$	12.2	19.7	—	—	CT	219
101	$CHCl_2COOH \cdot N(C_2H_5)_3$	21.7	54.4	7.28	5.8	B	48
102	$CF_3COOH \cdot O(C_4H_9)_2$	9.2**	20.5	4.25**	2.3	B	48
103	$CF_3COOH \cdot O(CH_2)_4$	11.8**	29.9	4.81	2.48**	B	48
104	$CF_3COOH \cdot OC(CH_3)C_2H_5$	9.5	23.4	5.38	2.30	B	220
105	$CF_3COOH \cdot OS(CH_3)_2$	13.2	24.5	6.39	2.18	B	220
106	$CF_3COOH \cdot SO_2(C_2H_5)_2$	8.3	18.8	6.33	1.62	B	220
107	$CF_3COOH \cdot SO_2(CH_2)_4$	8.0	18.1	—	—	B	220
108	$CF_3COOH \cdot ON(C_8H_7)_3$	28.3	76.5	11.5	7.3	B	220
109	$CF_3COOH \cdot ONC_5H_5$	16.0	32.6	8.21	4.8	B	220
110	$CF_3COOH \cdot OP(C_4H_9)_2CH_3$	15.7	35.2	7.34	3.1	B	220
111	$CF_3COOH \cdot OP(OC_4H_9)_3$	11.2	18.8	5.71	2.6	B	220
112	$CF_3COOH \cdot OP[N(CH_3)_2]_3$	15.5	26.2	—	—	B	220
113	$CF_3COOH \cdot OAs(C_8H_{17})_3$	22.0	49.6	9.19	3.57	B	220
114	$CF_3COOH \cdot N(C_2H_6)_3$	26.0	49.3	7.55	5.7	B	48
115	$CF_3COOH \cdot N(C_3H_7)_3$	25.7	—	8.38	6.5	B	48
116	$CF_3COOH \cdot N(C_4H_9)_3$	26.0	64.4	8.66	6.8	B	48
117	$CF_3COOH \cdot N(CH_3)_2C_6H_{11}$	26.8	69.5	7.38	5.4	B	48
118	$CF_3COOH \cdot NC_5H_5$	18.4	49.7	6.92	3.6	B	48
119	$CCl_3COOH \cdot O(C_4H_9)_2$	9.8	—	4.2**	2.14**		47
120	$CCl_3COOH \cdot O(CH_2)_4$	11.5**	28.7	4.86**	2.43**		47
121	$CCl_3COOH \cdot OS(CH_3)_2$	10.1	12.6	5.62	2.11	CT, B	219, 224
122	$CCl_3COOH \cdot OS(CC_6H_5CH_2)_2$	9.7	11.7	—	—	CT	219
123	$CCl_3COOH \cdot OS(C_6H_5)_2$	7.4	8.0	6.22	2.61	CT, B	219, 224
124	$CCl_3COOH \cdot OSe(C_6H_5)_2$	15.9	28.7	—	—	CT	219
125	$CCl_3COOH \cdot ONC_5H_5$	22.0	60.4	6.93	3.19	B	220, 224
126	$CCl_3COOH \cdot OP(C_8H_{17})_3$	17.3	—	6.17	1.9	CT	220
127	$CCl_3COOH \cdot OP(C_6H_5)_3$	13.9	24.5	7.1	3.15	CT, B	219, 224
128	$CCl_3COOH \cdot OAs(C_8H_{17})_3$	27.8	121.1	10.74	6.3	B	220
129	$CCl_3COOH \cdot N(C_2H_5)_3$	26.3	69.8	7.46	5.4	B	48
130	$CCl_3COOH \cdot N(C_3H_7)_3$	25.5	63.1	8.19	6.1	B	48
131	$CCl_3COOH \cdot N(C_4H_9)_3$	25.4	66.1	8.82	6.7	B	48
132	$CCl_3COOH \cdot N(C_5H_{11})_3$	24.7	—	9.04	7.0	B	48
133	$CCl_3COOH \cdot N(CH_3)_2C_6H_{11}$	25.6	67.4	7.45	5.2	B	48
134	$CCl_3COOH \cdot NC_5H_5$	17.9	46.6	7.57	4.12	B	48, 239
135	$CBr_3COOH \cdot N(C_2H_5)_3$	24.2	60.1	7.56	5.6	B	48
136	$C_4H_4NH \cdot N(C_2H_5)_3$	5.9	8.2	3.15	0.60	CH	56, 221, 166
137	$CF_3COOH \cdot OAs(C_2H_5)_3$	23.4	58.1	9.36	4.4	B	240
138	$CF_3COOH \cdot OAs(C_6H_5)_3$	20.1	45.1	—	—	B	240
139	$CF_3COOH \cdot SAs(C_2H_5)_3$	10.1	18.5	7.0	1.7	B	240
140	$CF_3COOH \cdot SAs(C_2H_5)_2C_6H_5$	8.5	15.7	—	—	B	240
141	$CF_3COOH \cdot SAs(C_2H_4)_2$ (n-$CH_3C_6H_4$)	9.1	15.4	—	—	B	240
142	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$CH_3OC_6H_4$)	9.5	16.6	—	—	B	240
143	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$C_2H_5C_6H_4$)	9.6	17.0	—	—	B	240
144	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-FC_6H_4)	8.5	15.1	—	—	B	240
145	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-ClC_6H_4)	8.0	13.7	—	—	B	240
146	$CF_3COOH \cdot SAs(C_4H_5)_2$ (n-BrC_6H_4)	8.0	13.8	—	—	B	240
147	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$NO_2C_6H_4$)	7.0	12.0	—	—	B	240
148	$CF_3COOH \cdot SAs(C_2H_5)_2$ (n-$CH_3COOC_6H_4$)	7.0	11.0	—	—	B	240
149	$CF_3COOH \cdot SAs(C_6H_5)_2C_2H_5$	5.4	9.0	—	—	B	240

* Abbreviations: B = benzene, H = hexane, HP = heptane, O = octane, ODCB = *o*-dichlorobenzene, T = toluene, CH = cyclohexane, CT = carbon tetrachloride.

** These data have been refined in relation to those quoted in the relevant literature (more accurate calculations, replacement of benzene by a more inert solvent—octane).

type *nv* and *nσ* is the so called compensation effect, i.e. a linear relation between ΔH^0 and ΔS^0. As shown previously[164], this relation is general for the complex-formation reactions A + B $\rightleftharpoons$ A.B and is described by the equation

$$-\Delta H^0 = -0.337\Delta S^0 + 3.1. \qquad (19)$$

A linear relation between ΔH^0 and ΔS^0 was also observed in series of hydrogen-bonded complexes having similar compositions[8,154].

The tabulated data, which cover a wide range of various hydrogen-bonded complexes, are illustrated in Fig. 1, in the form of a plot of ΔH^0 against ΔS^0. Evidently these results fit fairly satisfactorily on a single straight line, whose equation, found by the method of least squares, is

$$-\Delta H^0 = -(0.346 \pm 0.013)\Delta S^0 + (2.77 \pm 0.38). \qquad (20)$$

The correlation coefficient is r = 0.970.

Within the limits of the confidence intervals, the coefficients of Eqn. (20) agree with those of Eqn. (19). Consequently the values of ΔH^0 and ΔS^0 for hydrogen-bonded complexes obey the relation characteristic of typical EDA complexes, which demonstrates the identity of the mechanisms of the formation of both types of complexes. A theoretical justification of the linearity of the relation between ΔH^0 and ΔS^0 for the formation of donor-acceptor complexes has been obtained[164] and it has been shown that it is caused mainly by the changes in the intramolecular degrees of freedom on complex formation. The entropy of complex formation can be represented by a sum of two terms:

$$\Delta S = \Delta S_{\text{transl + rot}} + \Delta S_{\text{int}}. \qquad (21)$$

The first term of Eqn. (21) reflects the change in the degrees of freedom associated with the motion of molecules as rigid bodies and the second reflects the change in the intramolecular degrees of freedom. The contribution of $\Delta S_{\text{transl. + rot.}}$ is always negative, since the binding of two molecules, and in particular A–H and B molecules, in a complex leads to the loss of three translational and three rotational degrees of freedom. This contribution (50–55 e.s.u.) is almost independent of the stability and structure of the complex[164]. The appearance of six new vibrational degrees of freedom, accompanying the formation of the intermolecular bond, makes the dominant contribution to ΔS_{int}. This contribution is always positive and is greater the lower the energy of the donor–acceptor bond[164]. For this reason, the absolute negative entropy of formation of complexes increases with increase of their enthalpy of formation.

The equilibrium constants for the formation of hydrogen-bonded complexes are frequently used as a measure of their relative stability. Such estimates must be treated with caution. The existence of the so called "isoequilibrium temperature" which is equal to the slope of the ΔH^0–ΔS^0 linear plot, follows from the linear relation between the enthalpy ΔH and entropy ΔS.[164,165] At this temperature (346 ± 13°K or 73° ± 13°C), the equilibrium constants for all complexes obeying Eqn. (21) are similar. At temperatures below the isoequilibrium value, the equilibrium constants increase with the enthalpy of formation of the complexes. Above the isoequilibrium temperature, the opposite relation should hold. Hence it follows that only those values of K which have been obtained below the isoequilibrium temperature may be used for the estimation of the relative energies of the hydrogen bonds.

V. THE STRUCTURE OF HYDROGEN-BONDED COMPLEXES AND ESTIMATION OF THE POLARITY OF HYDROGEN BONDS

Extensive experimental data have accumulated on the dipole moments (DM) of molecular hydrogen-bonded complexes. The Debye method, in which the concentration dependence of the dielectric constants and densities or refractive indices of fairly dilute solutions of the test substances is measured in inert solvents, is the commonest method for the determination of dipole moments. The measurement of the dipole moments of complexes by the Debye method makes it necessary to take into account the equilibrium constants[28], which are either determined by an independent procedure or from dielectric constant measurements simultaneously with μ_c, requiring the use of special methods for the interpretation of the results[28,166-170]. The difficulties arising in the measurements of the dipole moments of hydrogen-bonded complexes in solution and the methods for their determination are similar to

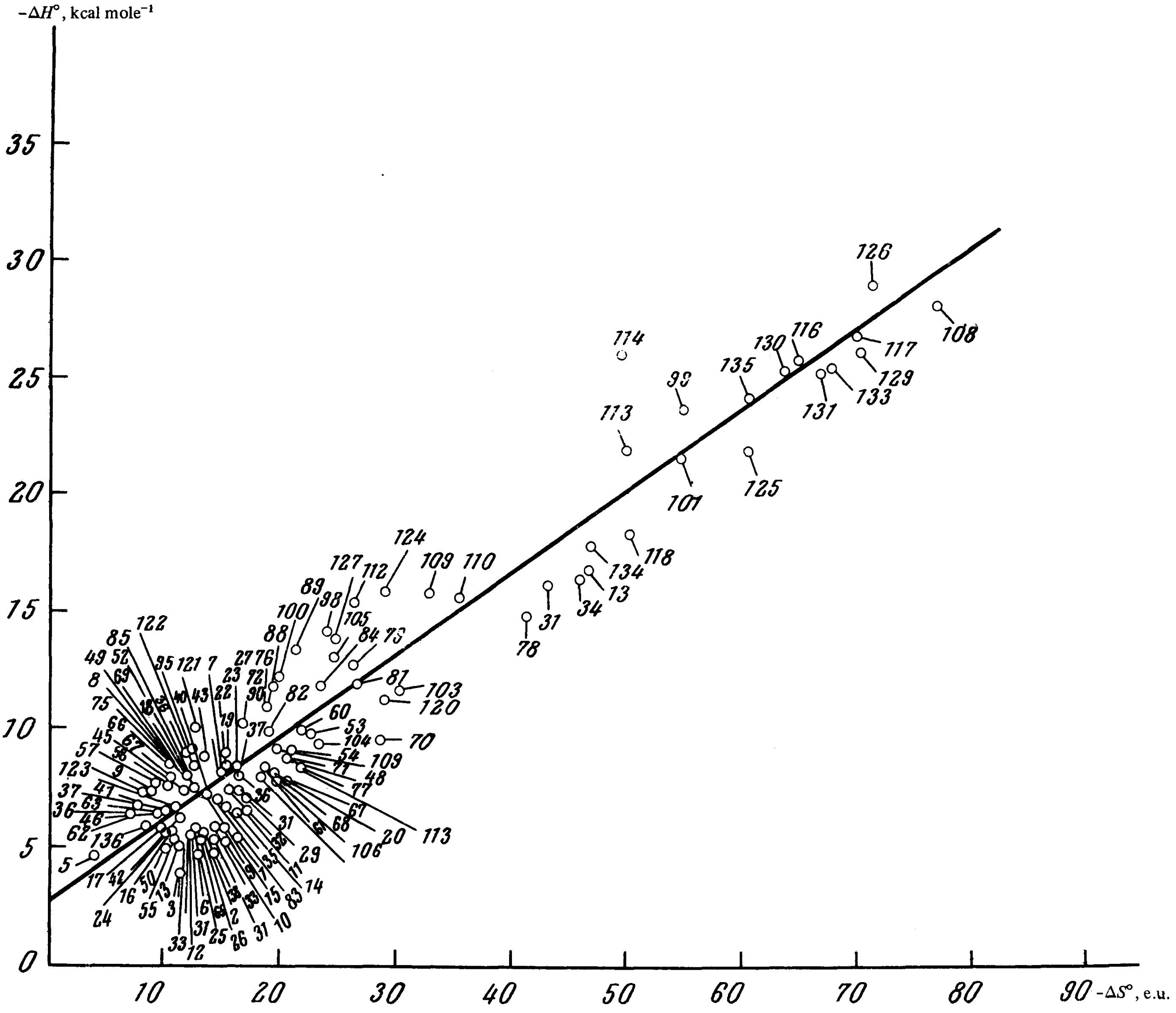


Figure 1. Relation between $-\Delta H^0$ and $-\Delta S^0$ for hydrogen-bonded complexes (the numbers of the points correspond to the numbers in the Table).

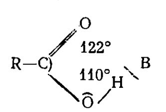
those described above for the determination of the thermodynamic parameters. The differences probably consist in the fact that, other conditions being equal, the values of μ_C are less sensitive to the influence of the solvent (naturally, comparatively inert solvents are considered) than the thermodynamic parameters. This is clearly shown, for example, by a comparison of the values of μ_C and ΔH^0 measured by the present authors[47,53] in benzene and octane for the complexes of 4-bromo- and 3,4-dimethyl-phenols with pyridine:

	Benzene		Octane	
	μ_C	$-\Delta H^0$	μ_K	$-\Delta H^0$
$4\text{-BrC}_6H_4OH \cdot NC_5H_5$	5.24	6.9	5.30	8.0
$3,4\text{-}(CH_3)_2C_6H_3OH \cdot NC_5H_5$	4.40	5.9	4.40	7.2

Within the limits of the present review, we are unable to give a compilation of all the measurements of the dipole moments of hydrogen-bonded complexes. We believe that the Table lists the most reliable dipole moments of such complexes. We may note that, in order to obtain information about the polarity of the intermolecular hydrogen bonds, one mainly considers the simplest systems in which the formation of the intermolecular hydrogen bond is not complicated by an additional interaction. Furthermore, compounds where the enthalpies of formation have been measured as well as their dipole moments are given preference.

Within the framework of the approximation of the vector additivity method for the determination of $\Delta\mu$ (the increment in the dipole moment of a hydrogen-bonded complex relative to the vector sum of the dipole moments of the components), it is necessary to know not only the values of μ_C, μ_{AH}, and μ_B, but also the angles between these vectors. The available literature data on the structures of hydrogen-bonded complexes are considered below in this connection.

Structure (I) is most probable for the 1 : 1 complexes of carboxylic acids with bases[46,171,172]:

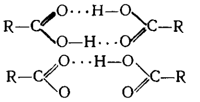


. (I)

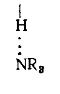
The planar conformation of the carboxy-group with the *cis*-disposition of the proton of the O–H group relative to C=O has been established by gas-phase electron-diffraction for the formic acid[173] and propionic acid[174] monomers. X-Ray diffraction studies on the 1 : 1 complexes of trichloroacetic acid with pyridine *N*-oxide[172] and of *p*-bromo- and *p*-chloro-benzoic acids with piperidine[175] have shown that the *cis*-conformation of the carboxy-group persists also in the hydrogen-bonded complexes. It was established that complex formation does not cause any significant changes in the structures of the electron donor and electron acceptor molecules, with the exception of the groups directly involved in the formation of the hydrogen bond[175]. This behaviour is characteristic of *nσ* complexes, particularly the complexes of halogens with *n* donors[28].

The orientation of the B molecules relative to the X–H...Y bond depends on a number of factors. For sterically unhindered compounds, it is determined primarily by the state of the orbital occupied by the free electron pair of the corresponding heteroatom. As in the formation of intermolecular bonds in donor–acceptor complexes, in the hydrogen-bonded complexes the principle of maximum overlap probably holds[28]. From this standpoint, the most probable structure of the complexes of carboxylic acids with amines and phosphines is one where the X–H...Y bond axis coincides with the symmetry axis of the R_3N or R_3P molecule (the sp^3 orbital of the lone electron pair of the heteroatom). In complexes with sulphides and selenides, the planes of the R_2S and R_2Se molecules are almost perpendicular to the X–H...Y axis (*p* orbital). In complexes with oxygen compounds, the angle between the plane of the donor molecule and the X–H...O axis is approximately 120°, which corresponds to the sp^3 hybridisation of the atomic orbitals of oxygen. However, this angle is not constant in different complexes, appreciable variations being observed[6,28,176].

The problem of the structure of the 2 : 1 complexes of carboxylic acids is still obscure. It has been shown that the hydrogen-bonded ring of the carboxylic acid dimer is planar and has a centre of symmetry[177–184] [structure (II)]. The dissociation of one of the hydrogen bonds in the dimer and the formation of a 3 : 1 complex are associated with significant changes in the conformation of the dimer. Analysis of the dipole moments of such carboxylic acid complexes with amines[48] leads to the conclusion that they most probably have conformation (III):



, (II)



. (III)

The changes in the structure of phenol molecules on complex formation are insignificant, as for carboxylic acids[192,193]. The orientation of the B molecules relative to the X–H...Y linkages in the complexes of phenols and alcohols was assumed to be the same as in the complexes of carboxylic acids. In the calculations of $\Delta\mu$, the same group dipole moments and valence angles were used as in earlier studies[47,48,171]. The calculated values of $\Delta\mu$ for the corresponding complexes are listed in the sixth column of the Table.

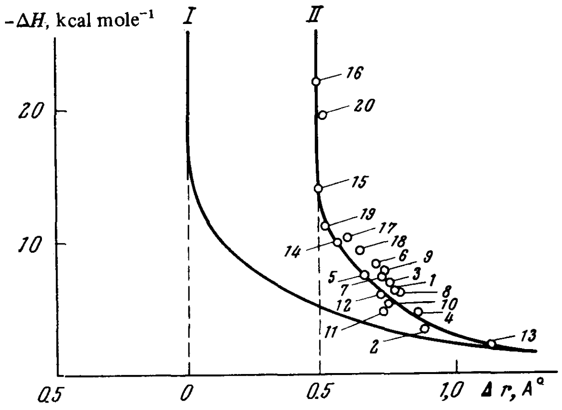


Figure 2. Relation between $-\Delta H^0$ and Δr: I) for typical EDA complexes; II) for hydrogen-bonded complexes; 1) $(CH_3OH)_2$;[226,231] 2) $[2,6\text{-}(CH_3)_2C_6H_3OH]_2$;[143,187] 3) $[3,4\text{-}(CH_3)_2C_6H_3OH]_2$;[142,191] 4) $(4\text{-}ClC_6H_4OH)_2$;[142,191] 5) $(HCOOH)_2$;[184,232] 6) $(CH_3COOH)_2$;[152,233] 7) $[(CH_3)_3.CCOOH]_2$;[184,234] 8) $(C_2H_5COOH)_2$;[151,235] 9) $(C_3H_7COOH)_2$;[184,236] 10) $(CCl_3COOH)_2$;[129,181] 11) $(H_3C\text{–}C{\equiv}C\text{–}COOH)_2$;[126,237] 12) $(C_6H_5COOH)_2$;[149,238] 13) 2,6-$(t\text{-}C_4H_9)C_6H_4.O(CH_2)_4$;[198] 14) 4-$ClC_6H_4OH.N(C_2H_5)_3$;[47,66] 15) $C_6H_5COOH.N(C_2H_5)_3$;[47,66] 16) $C_6H_5COOH.N(C_2H_5)_3$.[232,172]

The energies of the intermolecular hydrogen bonds vary over a wide range: from a few to several tens of kcal mole^{-1} (see the values of ΔH^0 in the Table). Appreciable differences in the X–H...Y bond lengths are observed at the same time. It was of interest to elucidate the relation between these most important parameters of hydrogen-bonded complexes. A relation between ΔH^0 and Δr (Fig. 2, curve I), where $\Delta r = r_{exp} - \Sigma r_{cr}$ is the difference between the experimental length of the donor–acceptor bond and the sum of the covalent radii r_{cr} of the atoms forming this bond, was obtained previously[194] for donor–acceptor complexes of type *nv* and *nσ*. For comparatively weak complexes, with enthalpies of formation up to 8–10 kcal mole^{-1}, there is a definite parallelism in the variation of ΔH^0 and Δr: the higher the intermolecular interaction energy the shorter the coordinate bond. The maximum approach of the molecules ($\Delta r = 0$) is reached for $-\Delta H^0$ = 14–16 kcal mole^{-1}. Consequently, when the enthalpy of formation of a particular complex of type *nv* or *nσ* reaches this value, one can assume with a fair degree of certainty that the length of the donor–acceptor bond in this complex is equal to the length of the corresponding covalent bond in conformity with Fig. 2 (curve I).

Naturally, owing to their mutual repulsion, the X, H, and Y atoms in systems with a hydrogen bond cannot form an X–H...Y linkage whose length is equal to the sum of the covalent radii r_X, $2r_H$, and r_Y. However, as in the EDA complexes, here too one may expect a limit to the approach of the molecules for a specific interaction energy. Fig. 2 (curve II) presents a plot of ΔH^0 against Δr for hydrogen-bonded complexes. Here $\Delta r = r_{exp} - \Sigma r_{cr}$, r_{exp} being the experimental X...Y distance in the A–H...B complex and $\Sigma r_{cr} = r_X + 2r_H + r_Y$. In order to plot ΔH^0 against Δr, the most reliable enthalpies of formation and interatomic distances in hydrogen-bonded complexes were used. Owing to the lack of experimental data, the results of quantum-chemical calculations were employed for systems 17–20; for systems 13–15, the bond lengths were obtained from the $\Delta\nu - r_{XY}$ correlation[66].

The fact that the nature of the relation between ΔH^0 and Δr for hydrogen-bonded complexes and EDA complexes is the same is most striking. In systems with comparatively weak hydrogen bonds (up to 10 kcal mole^{-1}), the values of Δr increase appreciably with increase of ΔH^0, but for stronger interactions Δr changes little. It is extremely remarkable that the limiting approach of the A–H and B molecules in hydrogen-bonded complexes is reached for approximately the same intermolecular interaction energy as in the usual EDA complexes.

It follows from the analysis of curve (II) in Fig. 2 that Δr is constant and approximately equal to 0.5 Å for complexes with an intermolecular hydrogen bond the enthalpy of formation of which exceeds 12–14 kcal mole^{-1}. Hence one may conclude that, in comparatively stable A–H...B complexes, the minimum X–H...Y distance within the limits of the approximations introduced, may be close to the sum $r_X + 2r_H + r_Y + 0.5$ Å.

The correlation between ΔH^0 and Δr proved extremely useful for the estimation of the intermolecular hydrogen bond lengths $r_{X...Y}$ from the ΔH^0 for the corresponding complexes. We have used it widely for the estimation of the degrees of charge transfer $\Delta\mu/er_{DA}$.

VI. RELATION BETWEEN THE DEGREE OF CHARGE TRANSFER AND THE ENERGY OF HYDROGEN BONDS

The most important evidence in support of the hypothesis that the intermolecular hydrogen bonds are of the donor–acceptor type is provided by the analysis of the relation between the degree of charge transfer and the energy of formation of hydrogen bonds. A linear relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ has been established[47,48] for a number of hydrogen-bonded complexes, mainly those of carboxylic acids and phenols. In the present review, we attempted to survey results referring to a wider range of systems, including the results of studies in recent years.

According to theoretical quantum-chemical calculations, the maximum fraction of the transferred charge is localised near the atom X in the X–H bond. One can assume to a first approximation that the charge is localised at the X atom. In this case, the distance r_{DA} over which the charge has been transferred and which is necessary for the calculation of $\Delta\mu/er_{DA}$ is equal to r_{XY}. We obtained the values of r_{XY} with the aid of a plot of ΔH^0 against Δr (Fig. 2, curve II) using the values of ΔH^0 for the corresponding complexes.

Fig. 3 shows a plot of the relation between the values of $\Delta\mu/er_{DA}$, calculated in terms of the $r_{DA} = r_{XY}$ approximation and the enthalpies of formation of the complexes listed in the Table. Evidently all the results fit fairly satisfactorily on a single straight line. Its equation is found by the method of least squares to be

$$-\Delta H^0 = (38.0 \pm 5.1)\frac{\Delta\mu}{er_{DA}} + (3.9 \pm 1.4). \qquad (22)$$

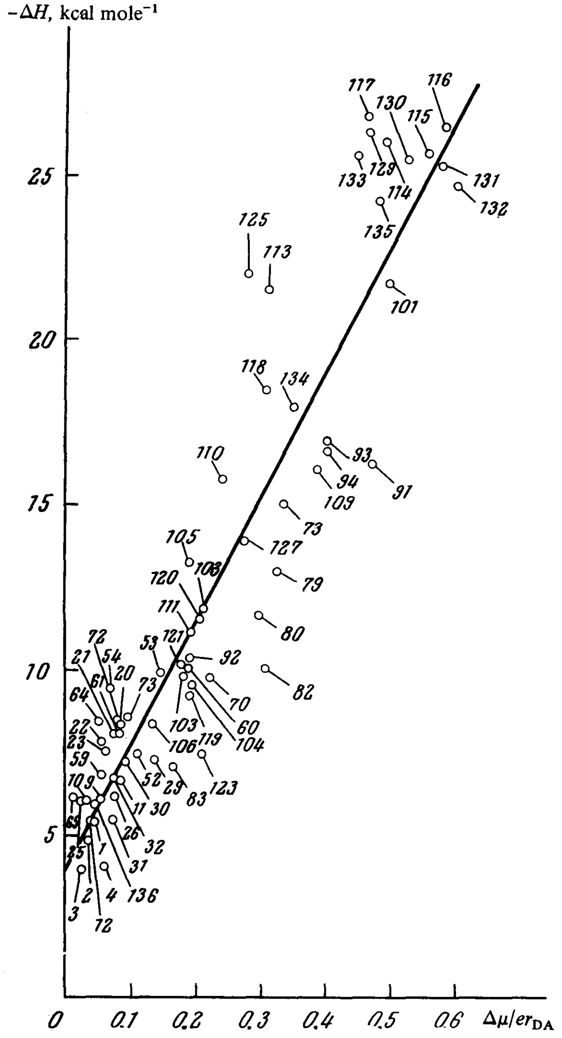


Figure 3. Relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ for hydrogen-bonded complexes (the numbers of the points correspond to the numbers in the Table).

The fairly high correlation coefficient (0.946) shows that, within the limit of the approximations adopted in the calculation of the degrees of charge transfer, one can postulate with a definite degree of certainty a linear relation between $-\Delta H^0$ and $\Delta\mu/er_{DA}$ for hydrogen-bonded complexes.

The linear correlation between the degree of charge transfer and the energy of intermolecular hydrogen bonds established on the basis of experimental data is consistent with Eqn. (13) derived from the equations of Mulliken's theory of charge-transfer complexes. According to Eqn. (13), the intercept which the linear plot of $-\Delta H^0$ against $\Delta\mu/er_{\text{DA}}$ makes on the ordinate axis is a measure of the energy of the intermolecular interaction via classical electrostatic forces. The value of 3–4 kcal mole^{-1} obtained in Eqn. (22) agrees fully with this hypothesis. The slope of the linear plot of $-\Delta H^0$ against $\Delta\mu/er_{\text{DA}}$ is equal, according to Eqn. (13), to the ratio of the energy of the charge-transfer band $h\nu_{\text{ct}}$ and the parameter A. The latter can be found from the dipole moment of the complex and the overlap integral for the interacting orbitals[49,61]. According to Eqn. (22), $h\nu_{\text{ct}}/A \simeq 1.6$ eV for hydrogen-bonded complexes. On the basis of this quantity and knowing the parameter A for the given complex, it is possible to estimate the position of the charge-transfer band in the electronic spectrum of this complex. The calculations showed that such bands for hydrogen-bonded complexes should occur in the far ultraviolet (below 200 nm).

It is remarkable that the slopes of the linear plots corresponding to Eqns. (1) and (22), which have a fully definite physical significance, agree within their confidence limits. Hence it follows that the relations between $-\Delta H^0$ and $\Delta\mu/er_{\text{DA}}$ for hydrogen-bonded complexes and typical EDA complexes are similar. This constitutes an experimental confirmation of the validity of the hypothesis, but there is no fundamental difference between the natures of the forces leading to the formation of both types of complexes.

The linear relation between the degree of charge transfer and the energy of intermolecular hydrogen bonds may be regarded as the most fundamental evidence for the donor–acceptor nature of the hydrogen bond, since this relation actually reflects the main features of the mechanism of the donor–acceptor interaction.

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Investigation of the ESR Spectra of Adsorbed Radical-ions as a Method for the Study of the Oxidation-reduction Properties of Zeolites

M.I.Loktev and A.A.Slinkin

The influence of the conditions in the preliminary heat treatment of zeolites, of the degree of elimination of metal cations and aluminium, and of the nature of the cation introduced and the adsorbed molecule on the oxidation-reduction properties of zeolites is examined. It is shown that the available experimental data support the model postulating the formation in zeolites of centres of different strengths, the activity of which in the formation of radical-ions is determined by the type of zeolite and the conditions in its preliminary treatment.
The bibliography includes 33 references.

CONTENTS

I. INTRODUCTION

The study of the nature of the acid–base centres in zeolites is a fundamental problem the solution of which is necessary for understanding the mechanism of the action of this most important group of catalysts. Studies on amorphous aluminosilicates have already shown[1] that, apart from the usual Lewis and Brønsted centres, the surfaces of these catalysts contain the so called oxidation and reduction centres, the adsorption on which of condensed aromatic systems involves a one-electron transfer, and not the transfer of an electron pair, with formation of the corresponding adsorbed radical-ions (Fig. 1). However, the nature of these centres is not yet clearly understood. Nevertheless studies in recent years have shown that the oxidation-reduction centres can play a significant role in acid–base reactions catalysed by aluminosilicates.

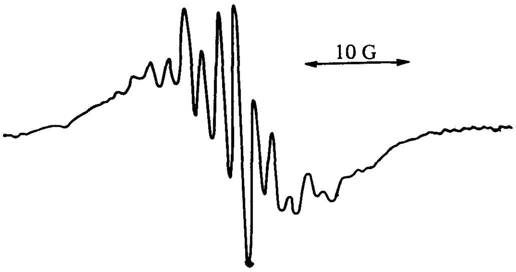


Figure 1. The ESR spectrum of anthracene adsorbed on an aluminosilicate from benzene solution[1].

The crystal structures of zeolites and the centres in these structures where cations may be located have now been quite thoroughly investigated. In recent years this situation stimulated detailed research on the oxidation-reduction centres in zeolites, which has led to new important generalisations in this field. The aim of the present review is to examine data obtained in studies, mainly by ESR, of the oxidation-reduction properties of different types of zeolites towards a wide variety of electron-donating and electron-accepting molecules.

It is not yet possible to classify the oxidation-reduction properties of zeolites according to any single characteristic of the adsorbent (the Si : Al ratio, the degree of elimination of cations or aluminium from the given type of zeolite) or according to the conditions in its preliminary treatment (heat treatment temperature, the amount of O_2 or H_2O determined). We shall therefore consider initially the oxidation-reduction properties of zeolites of types X and Y from which metal cations have been partly or completely eliminated. The review does not deal with studies in which the formation of radical-ions following the adsorption of hydrocarbons on zeolites has been observed under the conditions of external influences on the system, for example ultraviolet light or γ-radiation.

II. THE OXIDISING AND REDUCING PROPERTIES OF FAUJASITES

1. The Influence of the Degree of Elimination of Metal Cations, the Conditions in the Heat Treatment of Zeolites, and the Nature of the Adsorbed Molecule on the Oxidation-Reduction Properties of Faujasites

The adsorption of diphenylethylene, triphenylamine, quinoline, perylene, *p*-phenylenediamine, and aniline from 1 : 1 or 1 : 2 solutions in n-heptane or chloroform on type Y zeolites from which metal cations have been eliminated to different extents has been investigated[2]. The preliminary dehydration of the zeolite was carried out *in vacuo* at temperatures up to 500°C for 24 h. The substances were adsorbed in an atmosphere of pure N_2 at room temperature and the amount of adsorbed hydrocarbons was determined spectrophotometrically by measuring the concentration in the solution before and after the adsorption. Equilibrium in the adsorbate–zeolite system was attained after approximately 24 h. It was shown that the maximum degree of adsorption of triphenylamine on the NH_4Y zeolite activated at 500°C corresponds to 3.4×10^{20} molecules per gram of zeolite (one molecule per large cavity or approximately eight molecules per unit cell). The maximum number of triphenylamine radical-cations formed in the adsorption process is 1.2×10^{19} spins g^{-1}.

The authors[2] suggested that there exists definite steric hindrance to the approach of the $(C_6H_5)_2N$ molecule to the electron-accepting centre.

It is noteworthy that the concentration of neutral perylene molecules in the charge-transfer complexes formed in the perylene–iodine system[3] is also approximately 30 times higher than the concentration of the free perylene radicals produced. The alternative explanation is that the stabilisation of a single radical-cation formed may require several neutral molecules.

The influence of the temperature of activation of the zeolite towards adsorption and the formation of radical-ions has been studied for diphenylethylene[2]. It was observed that the equilibrium degree of adsorption of diphenylethylene, corresponding to ten molecules per unit cell of the zeolite, is already reached on the specimen activated at temperatures $\geqslant 200°C$. However, appreciable formation of radical-ions following adsorption was observed only on specimens heat-treated at approximately 400°C and the maximum concentration of radicals was noted on zeolites activated at temperatures $\geqslant 500°C$. In other words, for the adsorption of diphenylethylene it is sufficient to eliminate water molecules from the zeolite cavities, which occurs at 200°C, while the formation of electron-accepting centres requires higher activation temperatures (~400°C).

A similar dependence of the degree of adsorption and radical-cation concentration on the dehydration temperature of the NH_4Y zeolite was also observed for $(C_6H_5)_3N$. The degree of adsorption of $(C_6H_5)_3N$ is independent of the degree of elimination of metal cations from the type Y zeolite and corresponds to 3.4×10^{20} mol. g^{-1} or eight molecules per unit cell, which is characteristic of a specimen from which metal cations have been fully removed. However, the concentration of the triphenylamine radical-cations formed for low degrees of elimination of metal cations (up to 16 Na^+ ions from the unit cell) increases linearly with the degree of elimination of metal cations and the remains constant and equal to approximately 1.5×10^{19} spins g^{-1}.

It is known[4] that in the NaY zeolite unit cell 32 Na^+ ions are located in the plane of the six-membered oxygen rings (SII), 16 ions are in the hexahedral prisms (SI), and eight ions are in the large cavities (SIII). It has been suggested[2] that the exchange of only the first 16 Na^+ ions leads to the formation of electron-accepting centres. The centres formed in the course of the elimination of Na^+ ions from the S_{III} sites and partial removal from the S_{II} site, which are readily accessible to triphenylamine molecules, participate in the formation of radical-cations. However, it should be noted that a number of studies have now been published where a different distribution of Na^+ cations in NaY zeolites is suggested on the basis of X-ray diffraction data. In particular, some authors believe that 2–4 Na^+ cations remain non-localised (SIII) or that in general all the Na^+ cations in the unit cell are located at the S_I and S_{II} sites.

Assuming that the removal of only eight of the 56 Na^+ cations from the zeolite unit cell leads to the formation of active centres, Stamires and Turkevich[2] obtained 2.8×10^{20} centres g^{-1}, which is approximately 20 times more than the maximum number of the triphenylamine radical-cations formed (approximately 1.5×10^{19} spins g^{-1}). The possible causes of this discrepancy were discussed above. The determination of the spin–spin and spin–lattice relaxation times of the $(C_6H_5)_3N^+$ radical–cations adsorbed on the HY zeolite and measurements of the temperature dependence of the spin susceptibility for different concentrations of these radical-cations led to the hypothesis that associated species comprising neutral $(C_6H_5)_3N$ molecules, solvent molecules, and the radical-cations $(C_6H_5)_3N^+$ are formed and that there is equilibrium between the paramagnetic and diamagnetic molecules:

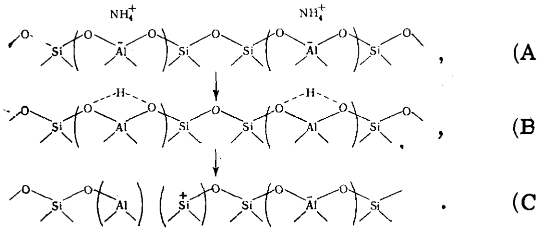
$$\underset{\text{2 radical-cations}}{2\,(C_6H_5)_3N^+} \rightleftarrows \underset{\substack{\text{diamagnetic}\\ \text{ion}}}{(C_6H_5)_3N^{2+}} + \underset{\text{neutral molecule}}{(C_6H_5)_3N + Q} \,.$$

The resolution of the hyperfine structure (HFS) spectrum of the triphenylamine radical-cation (triplet due to the ^{14}N nucleus with $I = 1$) depends on the number of $(C_6H_5)_3N$ molecules present in the zeolite pores which have reacted. It may be that this is associated with the interaction between $(C_6H_5)_3N^+$ and $(C_6H_5)_3N$ already mentioned, leading to the delocalisation of the unpaired electron and the disappearance of the HFS, or with the hindrance of the rotation of the radical by an excess of neutral molecules in the zeolite pores.

The influence of the solvent on the HFS of the $(C_6H_5)_3N^+$ ESR spectrum has been demonstrated by the following experiment. Triphenylamine was adsorbed from the gas phase at 200°C on a type Y zeolite from which metal cations had been eliminated and the ESR spectrum at room temperature was recorded at different time intervals (as the colour of the specimen changed). In all cases, a singlet line with slight asymmetry and a g-factor close to 2.00 was observed. The addition of n-heptane to zeolites at room temperature in a nitrogen atmosphere led to the immediate appearance of the HFS due to the nitrogen nuclei. On the other hand, the well resolved spectrum of the $(C_6H_5)_3N^+$ radical-cation adsorbed on the HY zeolite from solution in n-heptane is broadened and becomes anisotropic as a result of removal of the solvent or the reduction of the temperature at which the spectrum is recorded.

Stamires and Turkevich[2] noted that, in all cases where they observed a well resolved HFS of the spectrum of the adsorbed radical-cation, the subsequent adsorption of O_2 caused a reversible broadening of the ESR line. The fact that in the adsorption of the radical-cation the ESR method does not reveal the unpaired electron captured by the zeolite is probably due to the short relaxation time or the complete delocalisation of the electron in the zeolite lattice, where the varying crystal fields broaden the ESR line so much that it becomes impossible to observe.

It was shown[2] that iodine, one of the best acceptors in charge-transfer complexes, does not form these complexes at room temperature with donors such as aniline, naphthalene diphenylamine, and diphenylethylene, systems of this kind giving rise to an ESR signal only at elevated temperatures. Since the adsorption of the above substances on a zeolite freed from metal cations leads to the appearance of radical-cations already at room temperature, one may conclude that the electron-accepting centres of such an adsorbent exhibit at least the same activity as iodine. The following scheme for the formation of electron-accepting centres during the heat treatment of the NH_4Y zeolite was put forward on the basis of the results[2]:



Heat treatment of the ammonium-form of the zeolite leads to the formation of NH_3 and H^+ ions. The latter, interacting with the lattice oxygen, form the intermediate structure (B). With increase of heat-treatment temperature (~400°C), the elimination of OH groups begins, the latter giving rise to H_2O by reacting with H^+, and defects appear in the zeolite [structure (C)]. A complex involving charge transfer from an adsorbed molecule to a tricoordinate aluminium atoms is formed in the adsorption of triphenylamine. The stabilisation of the radical-cation produced is due to the rigid arrangement of the electron-accepting centres in the zeolite lattice. The formation of such centres probably does not disrupt the zeolite structure, since the degree of adsorption of triphenylamine is independent of the degree of elimination of metal cations and is equal to 3×10^{20} mol. g^{-1}, which is characteristic of the specimen freed from metal cations. The active centre with the tricoordinate aluminium atom possesses properties analogous to those of $SbCl_5$,[5] acting similarly to iodine, and is an electron trap. Such $(AlO)_{3/2}$ traps are distributed uniformly throughout the zeolite structure.

In the communication by the same workers, dealing with an ESR study of γ-irradiated zeolites of types X and Y, it is shown that such combined $(AlO)_{3/2}$ centres and traps capture the electrons liberated on γ-irradiation of the zeolite and a six-component HFS, due to the splitting of the levels of the captured electron in the field of the ^{27}Al nucleus ($I = 5/2$), is observed in the spectrum. The adsorption of $(C_6H_5)_3N$ from solution after γ-irradiation of a type Y zeolite freed from metal cations does not lead to the formation of triphenylamine radical-cations, since the electron-accepting centres have already been occupied by the electrons liberated by the γ-irradiation. However, annealing of the γ-irradiated preparations regenerates the active centres: the six-component spectrum of the captured electron vanishes and the spectrum characteristic of the $(C_6H_5)_3N^+$ radical-cation appears immediately after the adsorption of triphenylamine.

As will be shown below (subsection 2 of this Section), these results conflict with the data of Dollish and Hall[7], who observed the formation of the radical-cations of perylene when it was adsorbed on an irradiated HNaY zeolite (45% exchange).

It has been shown[8] that the hydrogen-form of a type Y zeolite (HY) possesses, after appropriate activation oxidation-reduction properties similar to those of Al_2O_3 or amorphous aluminosilicates. The authors investigated the formation of the radical-ions of tetracyanoethylene (TCE), 1,3,5-trinitrobenzene (TNB), *m*-dinitrobenzene (DNB), and perylene in the adsorption of these compounds from solutions in benzene on NaY, HNaY, and HY zeolites, Al_2O_3, and an industrial 13% $Al_2O_3-SiO_2$ catalyst. The specimens were subjected to preliminary activation in a stream of O_2 for 1 h at temperatures in the range 100° to 1000°C and, after cooling *in vacuo* and reheating in O_2 at a pressure of 20 cm, were conditioned for 16 h *in vacuo* (10^{-5} mmHg) at the given temperature.

Preliminary tests showed that the concentration of the TCE, TNB, and DNB radicals formed depends on the concentration in the solution and on the time of contact between the adsorbate and the catalyst. The dependence of the number of radicals on the concentration in the solution implies that an adsorption equilibrium is established between the adsorbate molecules in the solution and the corresponding radicals on the adsorbent surface. The slow increase of the concentration of radical-ions with time shows that the radicals are formed not only on the outer surface but also within the channels and cavities of the zeolite. The maximum concentration of the radicals was observed in adsorption from 0.1 M solution after contact for 48 h. Additional ultraviolet irradiation of the adsorbate solution—zeolite system for 1 h led to an increase of the concentration of radical-ions by a factor of 1.5 for TCE and by factors of 2 and 3 for TNB and DNB respectively. Ultraviolet irradiation probably increases the electron-donating activity of weak centres. Presumably the fraction of such centres increases with the electron-affinity of the adsorbed molecule. The effect of irradiation in the case of TCE, a fairly strong electron-acceptor, is therefore significantly smaller than for the relatively weak acceptors such as TNB and DNB. These results indicate a fairly wide range of energies of the electron-donating (reduction) zeolite centres. In all subsequent experiments, the concentration of the radical-ions formed was determined after keeping a 0.1 M adsorbate solution in contact with the zeolite for 48 h and after additional ultraviolet irradiation of the system for 1 h.

It has been shown[8] that the adsorption of TCE by the HY zeolite dehydrated at 150—400°C is accompanied by the appearance of a nine-line ESR spectrum with $g = 2.0027$ and an HFS constant of approximately 4.9 G, which is characteristic of the TCE radical-anion. At dehydration temperatures above 400°C, the HFS disappears and the observed singlet is analogous to the ESR signal of the TCE polymer[9]. The singlet is observed also in the adsorption of TCE on the NaY zeolite over the entire range of dehydration temperatures. The dependence of the concentration of the TCE radical-anions on the heat-treatment temperature of HY and NaY is characterised by two maxima in the region of temperatures of approximately 250° and 650°C.

Table 1. The concentration of TCE radical-anions (spins g^{-1}) on various adsorbents[8].

Activation temperature	Adsorbent			
	HY	NaY	Al_2O_3	13% $Al_2O_3-SiO_2$
250°	$3 \cdot 10^{17}$	$3.5 \cdot 10^{17}$	$4.5 \cdot 10^{18}$	$6.5 \cdot 10^{17}$
660°	$4.2 \cdot 10^{18}$	$3.1 \cdot 10^{17}$	$9.0 \cdot 10^{18}$	$9.8 \cdot 10^{17}$

Table 1 presents data characterising the reducing properties of the adsorbents investigated in the formation of TCE radical-anions.

It has been shown[8] that the concentration of TCE radical-anions is independent of the degree of exchange of Na^+ for NH_4^+ and amounts to approximately 3×10^{17} spins g^{-1} when the preliminary dehydration of the zeolite has been carried out at 250°C. However, a sharp non-linear increase of the concentrations of TCE, TNB, and DNB radical-anions, starting from 35% exchange, was observed on specimens activated at 650°C. It is interesting to note that the oxidising activity of the type Y zeolite in the formation of triphenylamine radical-cations[2] reaches a maximum for approximately the same degree of elimination of metal cations (approximately 30%), remaining constant on further increase of the degree of exchange. One cannot rule out the possibility that the removal of the first Na^+ ions leads mainly to the formation of oxidation centres and further elimination of metal cations (after approximately 30% exchange) is accompanied by a sharp increase of the number of reduction centres.

The oxidising properties of type Y zeolites have been studied[8] in relation to the adsorption of perylene from a saturated benzene solution (approximately 6.5×10^{-3} M) at room temperature. The maximum concentration of the perylene radical-cations was reached after the solution has been in contact with zeolite for 5 days and did not change after additional ultraviolet irradiation. In the presence of O_2, the adsorption of perylene on the HY zeolite at room temperature gives rise to an ESR spectrum characteristic of the perylene radical-cation. It was noted that the HFS of the spectrum and its relatively slight time variation are analogous to the changes observed in the adsorption of perylene on amorphous aluminosilicate.

The concentration of the perylene radical-cations depends almost linearly on the activation temperature of the HY zeolite over the temperature range 150–660^{c}C. The maximum concentration observed on the specimen activated at 660°C corresponds to approximately 1.7×10^{19} spins g^{-1} or approximately 3.1×10^{16} spins m^{-2}. The adsorption of anthracene under the same conditions involves the formation of a number of radical-cations smaller by a factor of approximately 4. This finding shows that the yield of radical-cations is determined mainly by the ionisation potential of the adsorbate molecule and not by its size (at least for perylene and anthracene). When the activation temperature exceeds 700°C, a sharp decrease of the concentration of perylene radical-cations is observed, being due to the disruption of the zeolite structure, which is revealed by X-ray diffraction.

Table 2.

Adsorbent	Concentration of TCE radical-anions, 10^{-15} spins m^{-2}	Concentration of perylene radical-cations, 10-15 spins m^{-2}
HY	8	31
Al_2O_3	45	7
13% Al_2O_3—SiO_2	3	2

Table 2 presents the oxidising and reducing activities of the HY zeolite, an amorphous aluminosilicate (13% Al_2O_3–SiO_2), and Al_2O_3 expressed in terms of the number of perylene radical-cations and TCE radical-anions referred to 1 m^2 of the adsorbent surface for an activation temperature of 660°C.

It is suggested that two types of reduction (electron-donating) centres exist on the HY surface. The relatively weak centres correspond to the activity maximum for an activation temperature of 250°C. These centres reduce the TCE molecules to the radical-cations, but are too weak to reduce the TNB and DNB molecules. It is significant that the activity of the weak centres is independent of the degree of exchange of Na^+ ions for NH_4^+. It is suggested[8] that such centres may be hydroxy-groups as happens in Al_2O_3 activated at low temperatures.

An increase of activation temperature to 660°C is accompanied by the dehydroxylation of the HY zeolite and leads to the formation of strong electron-accepting and electron-donating centres responsible for the oxidation-reduction properties of the zeolite, i.e. the mechanism is the same as that proposed by Stamires and Turkevich[2] (see above).

The fact that the maximum concentration of the radical-ions formed is significantly smaller than the possible number of oxidation-reduction centres is due, according to the authors[8], to the inaccessibility of some of these centres to the adsorbed organic molecules. It is postulated that, for low degrees of exchange (<35%), mainly Na^+ cations at the $S_{I'}$ sites, inaccessible to TCE molecules, are substituted and the activity of the HNaY zeolite in the formation of radical-anions does not therefore change. For degrees of exchange >35%, Na^+ ions at the S_{II} sites, accessible to TCE molecules, begin to exchange, which leads to a sharp increase of the reducing activity of the zeolite. However, subsequent investigations showed that this explanation is not the only one possible. It was shown previously[10] that the oxidising and reducing properties of activated Al_2O_3 are to some extent interrelated. It was of interest to discover whether this relation between the oxidising and reducing properties holds for zeolites.

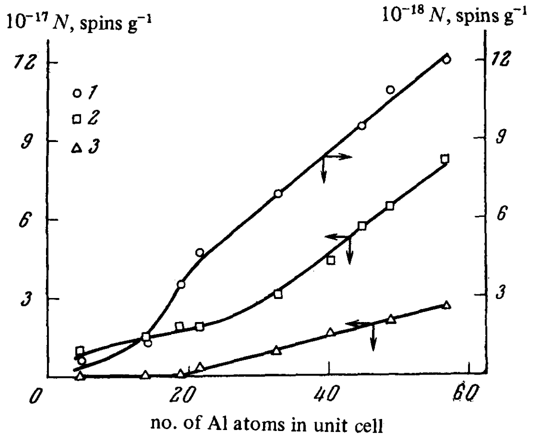


Figure 2. Variation of the concentration (N) of anthracene (curve *1*), TCE (curve *2*), and TNB (curve *3*) radical-ions with the number of aluminium atoms in the unit cell of a type Y zeolite[10].

A detailed study has been made[11] of the dependence of the oxidising and reducing properties of the HY zeolite on the Al : Si ratio. The adsorbates employed were 0.1 M benzene solutions of TCE, TNB, and DNB and 0.005 M benzene solutions of naphthalene, anthracene, and perylene. Fig. 2 illustrates the dependence of the concentration of the radical-ions of anthracene, TCE, and TNB on the number of aluminium atoms per unit cell of the type Y zeolite activated at 600°C. The decrease of the redox activity of the zeolite with decreased aluminium content is consistent, according to the authors, with the mechanism of the formation of electron-donating and electron-accepting centres already examined. The linearity of the plots in Fig. 2 shows that the activity of the zeolite is due to highly localised centres and not to the collective effect of several centres incorporating Al^{3+}.

We may note that this treatment of the experimental data is by no means self-evident. The point is that, even for maximum degrees of elimination of aluminium, the residual aluminium in the zeolite is quite sufficient for the formation of the same number of oxidation-reduction centres as in the specimens from which aluminium has not been removed. However, since the yield of radical-cations nevertheless falls with decrease of the aluminium content in the zeolite, one must suppose that not all the aluminium atoms in the crystal lattice are equivalent in relation to the formation of the oxidation-reduction centres. However, the aluminium elimination process is probably not homogeneous, i.e. some aluminium atoms are removed first. The linearity of the plots in Fig. 2 in such a case is rather unexpected.

It has been shown[11] that preliminary adsorption of anthracene and perylene on the HY zeolite causes a tenfold increase of the concentration of TNB radical-anions compared with the yield of these species in adsorption on a clean zeolite surface.

Almost the same increase of the yield of TNB radical-anions after the preliminary adsorption of electron-donating molecules (anthracene and perylene) was observed on the HY zeolite activated *in vacuo* and on the dealuminated HY zeolite. However, the effect is not observed when naphthalene is the first substance to be adsorbed. The preliminary adsorption of TNB likewise does not increase the yield of the anthracene radical-cations. Table 3 presents data illustrating the influence of the preliminary adsorption of various aromatic hydrocarbons on the yield of TNB radical-anions.

Table 3.

Adsorbate	Ionisation potential, eV	Maximum concn. of radical-cations per gram of zeolite	Average number of radical-cations required for the formation of one TNB radical-anion
Perylene	6.83	$5 \cdot 10^{19}$	2.7
Anthracene	7.23	$1{,}2 \cdot 10^{19}$	2.7
Naphthalene	8.1	$6 \cdot 10^{17}$	—
Benzene	9.25	$1 \cdot 10^{17}$	—

Evidently approximately one TNB radical-anion is formed additionally for each three anthracene or perylene radical-cations. This implies that only one of the three oxidation-reduction centres is involved in the increase of the yield of TNB radical-anions by virtue of its structure and energy relations. One can also suppose that the increased yield is due to the cooperative interaction of three neighbouring oxidation centres with one reduction centre. The latter hypothesis is supported by the finding that the increased yield is almost independent of the degree of elimination of aluminium from the zeolite.

Flockhart et al.[11] believe that such a large increase (by an order of magnitude) in the concentration of radical-anions as a result of the formation on the zeolite surface of radical-ions of opposite sign cannot be accounted for solely on the basis of the model proposed previously, which assumes that some of the active centres are inaccessible to the adsorbate molecules. A more likely hypothesis is that centres having different strengths exist. Possibly the observed tenfold increase in the concentration of radical-anions characterises the number of electron-donating centres whose strength is insufficient to reduce the TNB molecule to the radical-anion. The electron-donating capacity of such centres increases following the adsorption of anthracene or perylene on neighbouring oxidation centres. The independence of the increase in the yield on the degree of elimination of aluminium apparently shows that it is mainly aluminium atoms responsible for the strong electron-donating centres which are removed during the aluminium elimination process.

Naphthalene, which has a higher ionisation potential than anthracene and perylene, is adsorbed on energetically stronger oxidation centres, which do not interact with the nearest reduction centres. Preliminary adsorption of naphthalene does not therefore lead to an increase of the yield of TNB radical-anions.

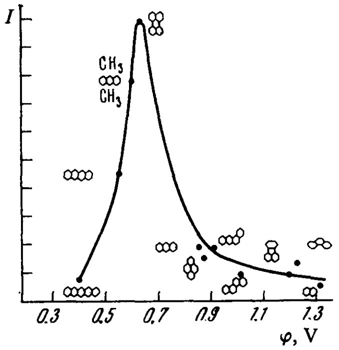


Figure 3. Variation of the integral ESR signal intensity (*I*) with the half-wave potentials (φ) of various aromatic hydrocarbons adsorbed on 22% Al_2O_3–SiO_2 (the potentials have been measured relative to Ag–0.1 *N* Ag^+ in acetonitrile)[11].

It is noteworthy that the conclusion concerning the formation of oxidation-reduction centres of different strengths had been made earlier[12], but in relation to amorphous aluminosilicates. The author obtained an experimental relation between the concentration of the radical-cations of different aromatic hydrocarbons formed in the experiment and the half-wave potential of the adsorbate (Fig. 3). He attempted to describe this relation theoretically and showed that the best agreement between the theoretical and experimental curves is observed when account is taken of the distribution of the oxidation centres of the aluminosilicate with respect to strength. Since such distribution is unknown *a priori*, the author postulated a Boltzmann distribution in the calculation of the theoretical curve. Furthermore, the possibility of the formation of doubly charged cations was postulated for adsorbates with low ionisation potentials (tetracene and pentacene).

2. The Nature of the Influence of Molecular Oxygen on the Formation of Radical-Ions

In the investigations discussed above[2,8,10], the problem of the influence of O_2 on the oxidising and reducing properties of zeolites was not specially studied. Flockhart and coworkers[8,10] carried out the preliminary heat treatment and the adsorption of hydrocarbons in the presence of O_2. Although Stamires and Turkevich[2] carried out the preliminary dehydration *in vacuo*, their method for the impregnation of the adsorbent with the adsorbate solution (in an atmosphere of dry nitrogen) did not rule out the access of traces of O_2 into the system.

Dollish and Hall[7] studied the influence of the preliminary heat treatment of the NH_4Y, NH_4X, NaY, and CaY zeolites and of O_2 on the yield of radical-anions in the adsorption of perylene and triphenylamine from benzene solutions. They investigated zeolite specimens activated in four different ways: (*a*) by evacuation at 550°C; (*b*) by heat treatment in a stream of O_2 for 17 h at 550°C with subsequent evacuation at the same temperature for 17 h; (*c*) by heat treatment in a stream of O_2 at 550°C with subsequent slow cooling in O_2 to room temperature and evacuation at room temperature; (*d*) by heat treatment in a stream of O_2, evacuation for 6 h, treatment in a stream of H_2 for 24 h, and evacuation for 6 h, all the treatments being carried out at 550°C. Table 4 presents the experimental data for the influence of the preliminary treatment of the zeolites on the yield of radical-ions. In all cases, the surface coverage by the adsorbate was 7×10^{20} mol. g^{-1} (4×10^{20} mol. g^{-1} for triphenylamine).

Table 4. The influence of the preliminary treatment of zeolites on the concentration of radical-ions (10^{17} spins g^{-1}).

Adsorbent, % exchange, adsorbate	NH_4Y			CaY		NH_4X*	NaY
	45%	79%	79%	36%	79%	48%	
Type of treatment	perylene	perylene	tri-phenyl-amine	perylene	perylene	perylene	perylene
a	1.3	6.2	1.0	0.3	0.6	0.3	not detected**
b	9.5	32.3	8.1	0.3	9.1	1.0	not detected
c	36***	58****	20****	0.4***	15***	2.6***	—
d	1.0	1.8	0.7	—	0.3	—	—

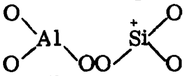
*Heat-treated at 500°C owing to its lower thermal stability.

**Exposure to dry air for 24 h leads to the appearance of a signal equivalent to 0.9×10^{17} spins g^{-1}.

***Exposure to air for 24 h does not alter the concentration of the radical-ions or alters it only slightly (≤15%).

****Exposure to air for 24 h increases the concentration to 1.2×10^{19} spins g^{-1}.

The influence of O_2 on the yield of perylene radical-cations was studied in detail on an NH_4Y specimen with 45% exchange, treated by method *a*. The results show that the adsorption of a single O_2 molecule induces the formation of a single perylene radical-cation. The same stoichiometry was obtained also from the determination of the amount of H_2O formed after the reduction with hydrogen (method *d*). In order to elucidate the nature of the chemisorbed oxygen, the NH_4Y specimen with 45% exchange, treated by method *a*, was irradiated by X-rays *in vacuo*. The ESR spectrum of this specimen consisted of the sextet characteristic of the electron captured by an aluminium-27 ion[6] and of the spectrum of the O_2^- radical-ion. The concentration of these species was 1×10^{16} and 4×10^{16} spins g^{-1} respectively. Contact between the irradiated specimen and the perylene solution led to the disappearance of both signals and the appearance of the spectrum of theperylene radical-cation equivalent to 1.3×10^{18} spins g^{-1}. Table 4 shows that the yield of the perylene radical-cations on a non-irradiated NH_4Y specimen with 45% exchange is 1.3×10^{17} spins g^{-1}. These data demonstrate the important role of the oxygen chemisorbed irreversibly at 550°C in the formation of radical-ions. Since ESR signals due to O_2^- are not observed on the non-irradiated specimens, the authors assume that oxygen is chemisorbed in the form of some other species. However, such oxygen must react with perylene to form the ion pair $Pn^{\cdot+}O_2^-$. Nevertheless, the formation of the radical-cations is not accompanied by the appearance of an ESR signal due to O_2^-, which is perhaps a common feature of all donor–acceptor systems.

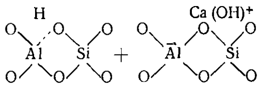
Dollish and Hall[7] discuss in detail the possible reasons why the maximum observed concentration of radical-cations is smaller by approximately two orders of magnitude than the number of anionic vacancies  in the 79% NH_4Y zeolite (approximately 1×10^{21} centres g^{-1}). Comparison of the sizes of the large cavities (approximately 13 Å), the diameters of the large channels (8–9 Å for NaY), and the sizes of the triphenylamine (approximately 10 Å) and perylene (6.5 × 9.1 Å) molecules led the authors to the conclusion that steric hindrance lowers the yield of radical-ions in the adsorption of such comparatively large molecules.

The influence of air and water vapour on the concentration of benzene, anthracene, naphthalene and diphenylamine radical-ions adsorbed *in vacuo* on a type Y zeolite from which cations have been removed has been investigated[13]. The preliminary treatment of the zeolite involved heat treatment for 4 h in air at 600°C followed by evacuation at 470–500°C. Benzene and naphthalene were adsorbed at room temperature and diphenylamine and anthracene at 85–90°C. It was shown that the ESR signal of the benzene radical-cation appears only after irradiation of the benzene molecules adsorbed on the zeolite with ultraviolet light for 20 h.

Naphthalene, anthracene, and diphenylamine radical-ions are formed without additional ultraviolet irradiation. It is suggested that the radical-ions are apparently formed via charge transfer to the electron-accepting centre formed when cations are eliminated from the zeolite, since adsorption on the metal cation-containing specimen does not lead to the formation of radical-ions. The formation of radical-ions from adsorbates with a high ionisation potential (benzene) requires an additional activation of the adsorbed molecule by ultraviolet radiation. The admission of water vapour gradually decreases the intensity of the ESR signals from anthracene and diphenylamine by a factor of 1.5–2. However, prolonged exposure of the specimen to water vapour does not lead to the complete disappearance of the signal. The influence of water has been explained by the reverse reaction involving the conversion of the radical-ion into a neutral molecule under the conditions of strong specific adsorption of water molecules by the zeolite. The admission of air increases the intensity of the ESR signals of the adsorbed anthracene and diphenylamine radical-ions which is probably due to the effect of oxygen.

3. The Influence of the Nature of the Cations and Their Location in the Zeolite Structure on the Oxidising and Reducing Properties of Faujasites

In the studies already mentioned[7-11], the formation of radical-ions was also observed on different cationic forms of zeolites of types X and Y. The appearance of an ESR signal (singlet) in the adsorption of TNB on CoY, NiY, and LaY has been noted[11]. The adsorption of TNB on CaY leads to the appearance of an ESR signal with a HFS. Dollish and Hall[7] investigated the influence of the degree of exchange of Na$^+$ for Ca^{2+} on the yield of perylene radical-cations. They found (Table 4) that, for low degrees of exchange ($\leqslant 36\%$), the activity of the CaY zeolite in the formation of radicals is very low even in the presence of O_2. However, for high degrees of exchange ($\geqslant 79\%$), the activity of CaY becomes comparable to that of the NH_4Y zeolite. For low degrees of exchange, Ca^{2+} ions occupy S_I sites in the hexagonal prisms connecting neighbouring cubo-octahedra and capable of accommodating 50% of the ions. Centres of another type are located in the plane (or close to it) of the six-membered rings in the large zeolite cavities. In the initial zeolite, there is on average one Na$^+$ ion for each ring of this kind. The complete exchange of the singly-charged Na$^+$ ions for the doubly-charged Ca^{2+} ions should lead to the formation of a positively charged centre and a centre with a partial negative charge (a cationic vacancy). In the presence of small amounts of water, the structure of the CaY zeolite can be represented schematically as follows:



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Dehydation results in the formation of centres in CaO analogous to those postulated for a type Y zeolite from which cations have been removed [see structure (C) in the scheme presented in Subsection 1 of the present Section].

A wider assortment of cationic forms of type Y zeolites was studied by Hirschler et al.[14] In order to elucidate the possibility of the formation of radical-ions on adsorption of molecules with a high ionisation potential (>9.0 eV), the authors studied the adsorption of olefins (oct-1-ene, pent-1-ene, etc.), benzene, and methylbenzenes on cationic forms of a type Y zeolite containing lanthanides as well as CaY and CeX. The zeolites were dehydrated in air at 500°C and the hydrocarbons were adsorbed from solutions in carbon tetrachloride. The authors concluded that the ESR spectra of the radical-cations observed in the adsorption of olefins cannot be accounted for solely by electron transfer from the adsorbed molecule to the adsorbent. On the basis of the gas-chromatographic analysis of the products of the reaction of pent-1-ene with the zeolite, the authors suggested that the radical-cations are formed from polymerisation products.

The influence of the amount and nature of the added cations on the ability of type X and Y zeolites to form radical-cations in the adsorption of anthracene and naphthalene has been investigated[15]. In addition to the sodium-form of the zeolites and the form freed from metal cations, a study was made of the magnesium, lanthanum, and yttrium cationic forms with different degrees of exchange. The zeolites were heat-treated for 6 h in a stream of dry air and then for 1 h in a stream of helium at 550°C. Naphthalene and anthracene were adsorbed from benzene solutions at room temperature. The formation of radical-cations in the adsorption on the NaY zeolite was not observed. In contrast to the results obtained by Hirschler et al.[14], Zhavoronkov[15] did not observe ESR signals in the adsorption of benzene on zeolites containing triply-charged cations. The adsorption of anthracene on cationic forms of a type X zeolite (with degrees of substitution of sodium by magnesium and lanthanum of 44 and 22% respectively) also did not lead to the appearance of an ESR signal. The latter result is, incidentally, not surprising, since the degree of substitution of cations was too low. The formation of radical-cations was observed in the adsorption of naphthalene and anthracene on type Y zeolites containing doubly- and triply-charged cations, the anthracene signal being more intense.

With increase of the degree of exchange of sodium for magnesium, lanthanum, and yttrium cations, the concentration of the radical-cations arising on adsorption of anthracene greatly increases, particularly on LaY and YY zeolites for degrees of exchange of 20–30%. In the range of 30–50% exchange, the concentration of radical-ions increases only slightly, but rises by an order of magnitude on passing to specimens obtained with non-equivalence of the exchange of sodium for triply-charged cations. Such non-uniformity in the increase of the concentration of the paramagnetic species as a function of the degree of exchange may be associated with the non-equivalence of various sites occupied by the sodium cations in the zeolite introduced by the exchange process. It is important to note that the concentration of the radical-ions formed on the specimen freed from cations and on zeolites with triply-charged cations for degrees of exchange in the range 20–30% are approximately the same, while for the magnesium-form the concentration is several times smaller. Zhavoronkov et al.[15] note different types of behaviour of X and Y zeolites with adsorbed anthracene in relation to atmospheric oxygen. Contact of type Y zeolites with air for several days hardly alters the concentration of the anthracene radical-cations formed. On the MgX, LaX, and NaY zeolites, radical-cations are also not formed immediately after adsorption, but exposure of these specimens to air for several days leads to the formation of paramagnetic centres at concentrations of 4.7×10^{16}, 5.7×10^{15}, and 1.6×10^{16} spins g^{-1} respectively.

Zhavoronkov et al.[15] do not discuss the role of the cations introduced into the zeolite in electron-transfer reactions. Richardson[16] and Neikam[17] investigated this problem. Richardson[16] used the ESR method to determine the degrees of ionisation of anthracene, naphthalene, perylene, and pyrene adsorbed on faujasites in which approximately 60% of the Na$^+$ ions had been replaced by K$^+$, Li$^+$, Ba$^+$, Sr^{2+}, Ca^{2+}, Mg^{2+}, Ag$^+$, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, or Cu^{2+} ions. The specimens were first dehydrated in air for 12 h at 400°C and the hydrocarbons were adsorbed from 0.01 M benzene solutions.

According to Richardson[16], the adsorption is accompanied by electron transfer from the adsorbate to the cation. The number of radical-cations varies exponentially with the difference between the ionisation energy of the adsorbate and the electron affinity of the cation. The conclusion that the cations are involved in the oxidation of anthracene to the radical-cation was reached on the basis of the following experiment. A series of specimens of the magnesium-form of the zeolite containing 2% of copper were heated for 2 h at 100°C. An ESR signal without the HFS characteristic of dehydrated Cu^{2+} ions was observed for these preparations and the adsorption of anthracene did not lead to the formation of radical-cations. The remaining specimens of this series were dehydrated at increasing temperatures and the ESR signals due to the Cu^{2+} ions were recorded also after the adsorption of anthracene. It was shown that the HFS characteristic of dehydrated Cu^{2+} ions and the spectrum of the anthracene radical-cations appear only after heat treatment above 300°C. The author's attempt to measure the changes in the intensity of the Cu^{2+} signal intensity due to electron transfer from anthracene to Cu^{2+} was unsuccessful, since the number of electrons involved in the reaction is too low to cause an appreciable decrease of the Cu^{2+} signal.

However, this experiment probably cannot be regarded as a direct confirmation of the involvement of cations in the oxidation of anthracene to the radical-cation. The results indicate only an agreement between the dehydration temperatures necessary, on the one hand, for the appearance in the spectrum of the HFS due to the Cu^{2+} ions and, on the other hand, for the formation in the zeolite of centres capable of oxidising anthracene. We believe that there are no grounds in this instance for the hypothesis that the changes in the environment of Cu^{2+} ions on dehydration, accompanied by the appearance of the HFS, need necessarily lead to the formation of anthracene radical-cations.

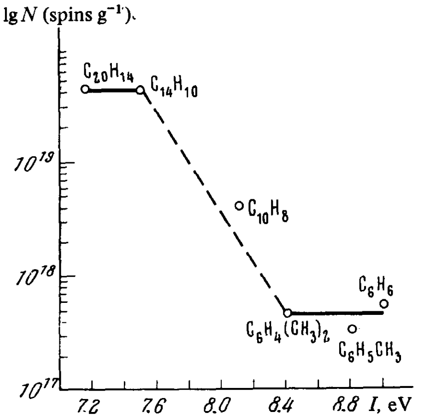


Figure 4. The yield of radical-ions (lg$N$) on the 13.3% CeY zeolite as a function of the ionisation potential of the adsorbate[17].

Neikam[17] investigated the activity of the lanthanide cationic forms of type Y zeolites in the formation of benzene, toluene, *p*-xylene, naphthalene, anthracene, perylene, and coronene radical-ions. The hydrocarbons were adsorbed from solutions in carbon tetrachloride on the zeolite activated at 500°C in air or in an oxygen atmosphere. It was shown that the concentration of the radical-ions formed following adsorption on the CeY zeolite is approximately an order of magnitude higher than on the LaY, SmY, and DyY zeolites. The adsorption on GdY leads to the appearance of very weak ESR radical-ion signal ($<10^{16}$ spins g^{-1}). The important role of O_2 in the formation of active centres was demonstrated by comparative experiments in which the 13.3% CeY zeolite was activated in helium, molecular hydrogen, or air. Fig.4 illustrates the variation of the logarithm of the concentration of the radical-ions (for the 13.3% CeY zeolite) with the ionisation potential of the adsorbed molecule.

The theoretical interpretation of this relation is based on the hypothesis[16] that the concentration of the radical-cations formed on adsorption ($N^{\dot{+}}$) obeys the Boltzmann distribution: $[N^{\dot{+}}] = N_0 e^{-\Delta E/kT}$, where N_0 is the number of adsorbed molecules and $\Delta E = I + A + W$. The ionisation potential of the adsorbate (I), the electron affinity of the adsorbent (A), and the charge-transfer energy (W) correspond to the following processes: $Ar \rightarrow Ar^{\dot{+}} + e(I)$ $S^{+} + e \rightarrow S(A)$, and $S + Ar^{\dot{+}} \rightarrow S \ldots Ar^{\dot{+}}(W)$. S and R denote the adsorbent and adsorbate respectively. It is readily seen that, when A and W vary only slightly for different adsorbates, the relation between lg$[N^{\dot{+}}]$ and I should be linear. Physically, this implies the energetic homogeneity of the electron-accepting zeolite centres.

The data presented in Fig.4 show that this is not the case. The presence of two regions with a constant concentration of the radical-cations formed, separated by a transition region, demonstrates the energetic inhomogeneity of the electron-accepting zeolite centres. It follows from Fig.4 that approximately 4×10^{17} centres in the 13.3% CeY zeolite have sufficient energy for the oxidation of molecules with $I \leqslant 9.0$ eV and approximately 4×10^{19} centres are capable of oxidising molecules with $I \leqslant 7.5$ eV. Centres of the third type correspond to the oxidation of naphthalene ($I \simeq 8.1$ eV). The author[17] explains on the basis of this model the similarity of the concentrations of anthracene and perylene radical-cations oxidised by centres with energy $\leqslant 7.5$ eV. Such agreement is also observed for benzene, toluene, and *p*-xylene, which may be oxidised to radical-cations only on centres whose energy is approximately 9.0 eV. We may note that the concentration of perylene radical-cations on a type Y zeolite freed from cations is approximately four times higher than the number of anthracene radical-cations[8] (Table 3).

The distribution of active centres with respect to energies depends on the cerium content in the zeolite. A decrease of the cerium content from 13.3% to 8.7% reduces the number of weak centres (7.5 eV) by a factor of 4 and the number of strong centres (9.0 eV) by a factor of 50. ESR signals were not observed in the adsorption on the 8.7% CeY zeolite of molecules whose ionisation potential is higher than that of naphthalene. On the basis of these data and the measurements of the magnetic susceptibility of the CeY zeolites, the author[17] concludes that the strong electron-accepting centres (9.0 eV) are distributed within the small cavities of the zeolites and include a pair of Ce^{4+} cations. However, it is suggested that the Ce^{4+} cations themselves, formed from Ce^{3+} when the zeolite is heat-treated in the presence of O_2, do not function directly as electron acceptors. The role of the Ce^{4+} cations reduces to an increase in the electron affinity of the active centres already formed in the zeolite under the influence of chemisorbed oxygen during heat treatment.

Fig.5 and the data in Table 5 illustrate the relation between the concentrations of the radical-cations formed and the number of adsorbed molecules. For perylene, curves *1* and *2* in Fig.5 coincide.

Comparison of the sizes of the adsorbed molecules with the diameters of the windows in the large zeolite cavities (7.5 Å) and allowance for the yield of the radical-cations led Neikam[17] to the conclusion that the weak oxidation centres (7.5 eV) are located on the outer zeolite surface. The low concentration of the coronene radical-cations (compared with perylene) indicates, according to the author, that the size of the adsorbed molecule is an important factor in the formation of radical-cations also in adsorption on the outer surface. The author believes that the results obtained by Stamires and Turkevich[2] for a type Y zeolite from which metal cations had been eliminated also confirm the conclusion that the oxidation centres are located on the outer surface.

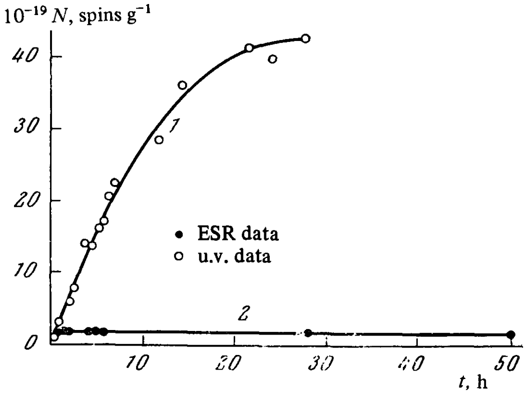


Figure 5. Variation of the degree of adsorption of anthracene and the concentration of the radical-cations formed (N) with contact time (t): 1) degree of adsorption based on the analysis of ultraviolet spectra; 2) the concentration of radical-cations based on ESR data (13% CeY zeolite)[17].

Table 5.

Molecular size	N_0	$[N^{+\cdot}]$, spins g^{-1}	$[N^{+\cdot}]/N_0$
Anthracene, 6 Å	$5.05 \cdot 10^{20}$	$4.17 \cdot 10^{19}$	1:12
Perylene, 7.7 Å	$4.37 \cdot 10^{19}$	$4.34 \cdot 10^{19}$	1:1
Coronene, 10.4 Å	$1.63 \cdot 10^{19}$	$6.8 \cdot 10^{17}$	1:11.4

This conclusion conflicts with probably all the previous experimental data obtained for zeolites. It is unlikely that the difference of almost two orders of magnitude between the concentrations of the perylene and coronene radical-cations (Table 5) is caused solely by the difference between the sizes of these species, if adsorption on the outer surface alone is postulated. This is particularly true, since Dollish and Hall[7] assume that the size of the windows in the large type Y zeolite cavities is 8–9 Å and not 7.5 Å as in Neikam's study[17]. It is apparently not permissible to reach such far-reaching conclusions solely on the basis of small differences between the dimensions of the perylene molecule (7.7 Å) and the inlet windows of the zeolite (7.5 Å). As will be seen below, in cases where the difference between the dimensions is large (in the adsorption of perylene on H-mordenite), the formation of radical-cations is not observed.

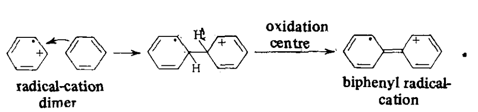
III. THE OXIDISING AND REDUCING PROPERTIES OF MORDENITES

1. The Characteristics of the Formation of Radical-ions on Mordenites

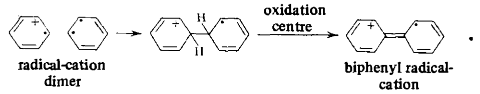
Analysis of studies on the oxidising and reducing properties of zeolites of types X and Y has shown that the adsorption of hydrocarbons with a high ionisation potential (approximately 9.0 eV) on zeolites of this type under normal conditions does not lead to the formation of the corresponding radical-cations. Naturally, we are not considering studies in which the formation of radical-ions was observed after additional treatments of the zeolite–adsorbate system, say, after ultraviolet irradiation. The formation of benzene, toluene, and *p*-xylene radical-cations has been observed[17] after adsorption on the CeY zeolite. However, no data concerning the nature of the ESR spectra (with the exception of the concentration of the radicals formed) are quoted in this report. Other workers[10,14] have also merely stated that weak and poorly resolved ESR spectra appear in the adsorption of benzene and its methyl derivatives on certain cationic forms of zeolites of types X and Y. The interpretation of these spectra is extremely difficult. After the publication of the first communications[18,19] about the ESR spectra of the radical-cations of benzene and its methyl derivatives, observed when they are adsorbed on a synthetic mordenite, there was a sharp growth of interest in the study of the oxidising and reducing properties of zeolites of this type. The point is that only on mordenites under normal conditions is the adsorption of hydrocarbons with a high ionisation potential (benzene, toluene, and xylene) accompanied by the appearance of intense ESR spectra with a well resolved HFS, which make it possible to identify the radical-cations formed on adsorption.

The study by Corio and Shih[18] is probably to be regarded as the first investigation in which an attempt was made to interpret the ESR spectra appearing after the adsorption of benzene and its methyl derivatives on the hydrogen-form of mordenite. The preliminary treatment of H-mordenite consisted in heating for 1 h at 500°C in an atmosphere of oxygen with subsequent evacuation for about 3 h at the same temperature. Liquid hydrocarbons were adsorbed at room temperature and solid hydrocarbons were fused and mixed with the zeolite. The ESR spectra were recorded at room temperature. Immediately after the adsorption of benzene on H-mordenite, the ESR spectrum consists of at least 7 HFS components and its overall width is approximately 30 G. The splitting between the components in the central part of the spectrum is approximately 2.2 G immediately after adsorption, increasing to approximately 3.8 G when 1 h has elapsed since the adsorption of benzene. Corio and Shih[18] assume that a radical-cation dimer, in which the unpaired electron is delocalised over the two benzene rings arranged in the form of a sandwich, is formed immediately after the adsorption of benzene. The subsequent time variation of the ESR spectra is due to the rapid establishment of equilibrium between the dimeric and monomeric forms of the radical-cations.

Other workers also concluded that the radical-cation dimers of benzene are formed when it is adsorbed on H-mordenite[19]. In this investigation the ammonium-form of mordenite was subjected to a preliminary heat treatment for 18 h in air at 520°C. The authors[19] reached the following conclusion on the basis of the time variation of the ESR spectra appearing after the adsorption of a 1.8 M benzene solution in carbon tetrachloride on H-mordenite and a comparison of these spectra with the spectrum obtained after the adsorption of a 0.1 M solution of biphenyl in n-hexane. The ESR spectrum observed immediately after the adsorption of pure benzene results from a superposition of the spectra of the benzene radical-cation dimer and the biphenyl radical-cation. At room temperature the spectrum of the dimer disappears after approximately 24 h and that of the biphenyl radical-cation (HFS constants of 6.74, 3.37, 0.52 G) remains. The adsorption of toluene and *o*-xylene under analogous conditions leads to the appearance of ESR spectra characteristic of the corresponding biphenyl radical-cations (the 4,4′-dimethylbiphenyl radical-cation for toluene and the 3,4,3′,4′-tetramethylbiphenyl radical-cation for *o*-xylene). The formation of toluene and *o*-xylene radical-cation dimers was not observed. Kurita et al.[19] postulate two mechanisms for the formation of biphenyl radical-cations when the benzene cation and neutral molecule react on an oxidation centre of H-mordenite. The ionic mechanism is as follows:



In methylbenzenes, the interaction may be between the carbon atom with the maximum positive charge in the cation and the carbon atom with the maximum negative charge in the neutral molecule. The second, radical mechanism is



In methylbenzenes, the interaction via the radical mechanism can occur between the carbon atom having the maximum spin density in the cation and the carbon atom having the maximum free valence in the neutral molecule. However, calculations by the simple Hückel method of the charge, spin density, and free valence in the cations and neutral molecules of toluene and *o*-xylene did not enable the authors[19] to make a choice between the radical and ionic mechanisms.

A more detailed analysis of the temperature variation (in the range 77–300 K) of the ESR spectra of tetramethylethylene and cyclopentene adsorbed on H-mordenite has been described by Corio and Shih[20]. The methods used in the preliminary treatment of the zeolite and in the adsorption of the hydrocarbons were the same as in their earlier study[18]. They showed that the activation energy for the rotation of cyclopentene on the surface of H-mordenite is 1.4 ± 0.2 kcal mole^{-1}. Such a low activation energy indicates virtually free rotation of the adsorbed cyclopentene molecule.

In the studies quoted above[18-20], the formation of radical-cations in the adsorption of various hydrocarbons (mainly aromatic hydrocarbons) on H-mordenite was postulated. However, the study of the ESR spectra of C_3–C_5 olefins adsorbed on H-mordenite led Leith[21] to a different conclusion. He showed that the adsorption of propene at room temperature on H-mordenite evacuated for 12 h at 450°C and then treated in oxygen at the same temperature leads to the appearance of an ESR spectrum consisting of 19 HFS components with a splitting of 8.1 G. Analogous spectra were observed also in the adsorption of but-1-ene and pent-1-ene. Fig. 6 presents the experimental spectrum of the adsorbed propene and its theoretical interpretation (a superposition of a triplet with the HFS constant $a_1 = 33.6$ G, a quintet with $a_2 = 16.8$ G, and a triplet with $a_3 = 8.1$ G). This spectrum does not correspond to the propene radical-cation, the formation of which would have been extremely difficult in any case owing to the high (9.73 eV) ionisation potential of propene. Leith[21] suggests that the observed ESR spectrum is due to the formation of the allyl radical

$$\mathrm{CH_3{-}CH \overset{\cdots}{-} \dot{C}H \overset{\cdots}{-} CH{-}CH_2{-}CH_3}.$$

The triplet with $a_1 = 33.6$ G was assigned to the splitting of the energy levels of the unpaired electron at the β-proton and a proton in the methyl group. The quintet with $a_2 = 16.8$ G was assumed to be due to the interaction with two α-protons, the β-proton, and another proton of the methyl group. Finally, the triplet with $a_3 = 8.1$ G was attributed to the interaction with the central proton of the allyl group and the remaining proton in the methyl group. Bearing in mind the identity of the ESR spectra from adsorbed propene, but-1-ene, and pent-1-ene, it is suggested that the olefin is dimerised after adsorption with subsequent abstraction of a hydrogen atom and the formation of the allyl radical.

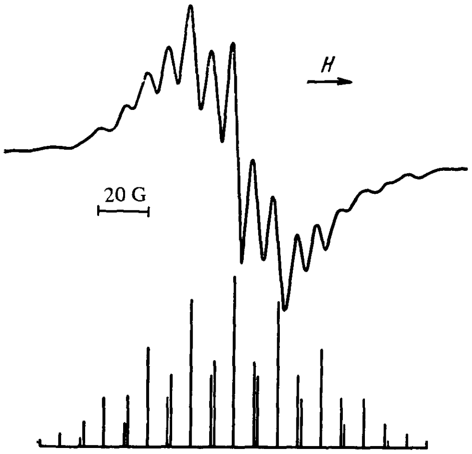


Figure 6. The ESR spectrum of propene adsorbed on H-mordenite and its theoretical interpretation[21].

2. The Influence of Heat Treatment and the Role of Chemisorbed Oxygen

The important role of oxygen in the formation of radical-ions following the adsorption of hydrocarbons on amorphous and crystalline aluminosilicates has been demonstrated in a series of studies. The problem has been investigated in relation to mordenites[22,23], a detailed study[22] having been made of the influence of the vacuum heat treatment of H-mordenite as well as the influence of H_2 and O_2 on the yield of benzene radical-cations. H-mordenite was first heated in air for 16 h at 500°C and then rehydrated for several days in a moist atmosphere. The standard heat treatment consisted in evacuation for 16 h at the given temperature in the range 100–800°C.

The treatment in hydrogen included the following stages: contact with H_2 at a pressure of 1 atm for 15 min at the standard heat treatment temperature and evacuation of H_2; repeated contact with H_2 under the same conditions with its subsequent evacuation for 3 h and cooling of the specimen *in vacuo*. Fig. 7 illustrates the influence of the temperature of the standard heat treatment of H-mordenite on the yield of benzene radical-cations (when 0.5 ml of benzene is adsorbed on 1 g of the zeolite) and on the specific surface of the zeolite determined by the BET method at 77 K from the adsorption of N_2. The weak maximum near 400°C can be attributed to the inaccuracy of the determination of the concentration of the radical-cations (errors of ±10%). However, it appears that the experimental error is not the real cause, since the changes in the concentrations of radical-cations on specimens evacuated at 300° and 500°C and treated in hydrogen are significantly different (Table 6). This finding probably indicates the formation of two different types of oxidation centres in specimens treated at 300° and 500°C respectively.

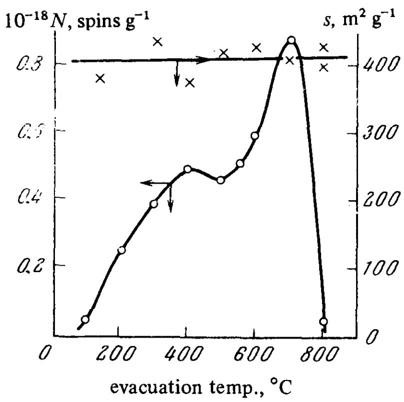


Figure 7. The influence of the heat treatment of H-mordenite on the concentration of benzene radical-cations (N) and the specific surface of the zeolite (s, determined by the BET method)[22].

The maximum number of benzene radical-cations is reached in the adsorption of 0.1 ml of benzene per gram of H-mordenite. The total adsorption capacity with respect to benzene at 25–28°C corresponds to approximately 0.09 ml per gram of zeolite. Consequently the maximum yield of the radical-cations is observed only when the mordenite channels are fully saturated by benzene. It must be emphasised that under these conditions approximately only 0.1% of the adsorbed molecules are oxidised to the radical-cations.

The data in Table 6 illustrate the influence of O_2 on the concentration of the radical-cations formed. It is evident from a comparison of these results with those presented in Fig. 6 that a particularly marked increase in the concentration of the radical-cations under the influence of O_2 is observed on the specimen evacuated at 800°C. The authors[22] showed that the ratio of the maximum number of radical-cations (2.1×10^{18} spins g^{-1}) and the number of O_2 molecules chemisorbed after treatment in hydrogen is 1 : 1.2. The treatment in hydrogen probably removes the most strongly chemisorbed oxygen remaining in the zeolite after the standard treatment. The evacuation of the O_2 adsorbed at room temperature and a pressure of 745 mmHg before the admission of benzene reduces the yield of radicals by approximately only 30% compared with the yield in the presence of O_2. Consequently chemisorbed by not physically sorbed oxygen plays an important role in the formation of the radical-cations. It is suggested that the chemisorption of an O_2 molecule on an H-mordenite active centre (or close to it) leads to the formation of a strong electron-accepting centre capable of oxidising benzene to the radical-cation. The yield of the radical-cations is limited by the amount of chemisorbed oxygen.

Table 6. The influence of treatment in hydrogen and of the oxygen pressure on the concentration of radical-cations formed.

Evacuation temperature, °C	Treatment in hydrogen	O_2 pressure, mmHg	Concentration of radical-ions, 10^{-17} spins g^{-1}
550	no	2.7	21.0
550	no	9.5	17.5
550	no	11.0	20.4
800	no	6.0	6.19
300	yes	0	1.18
500	yes	0	<0.01

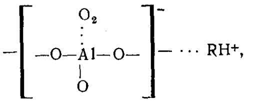
It was shown on the basis of the estimates quoted in the report of Sagert et al.[22] that only one mordenite unit cell in 100 contains a strong oxidation centre. The exact nature of these centres is unknown, but their formation is probably associated with mordenite crystal lattice defects. These centres are located in the principal mordenite channels. This conclusion is confirmed, on the onehand, by adsorption measurements and, on the other, by experiments with perylene. In the adsorption of perylene, which has a significantly lower ionisation potential and a larger molecular size than benzene, the authors[22] failed to observe the formation of radical-cations. According to other data[24], approximately 20% of the overall adsorbed species are located on the outer surface of mordenite. Thus the absence of perylene radical-cations shows that the oxidation centres are located within the mordenite structure and not on its outer surface.

More definite conclusions about the nature of the oxidation centres of mordenite responsible for the formation of benzene radical-cations were reached by Tokunaga et al.[23], who also investigated the influence of the preliminary heat treatment and the adsorption of O_2 and SO_2 on the yield of the radical-cations of benzene in its adsorption from the gas phase on NH_4Na-mordenite with a degree of exchange of 32%. It was shown that the benzene radical-cations are formed only after the evacuation of the zeolite at temperatures of the order of 500°C and that their concentration increases almost by an order magnitude with increase of the vacuum heat treatment temperature to 700°C. The parameters of the ESR spectrum and its time variation are analogous to those described by Kurita et al.[19] and correspond to the formation of benzene radical-cation dimers, which are converted after a time into biphenyl radicals. The yield of benzene radical-cations increases by a factor of approximately 5 as a result of the subsequent adsorption of O_2 at room temperature after the removal of benzene from the gas phase. The increase of the concentration of radicals has also been observed when O_2 was adsorbed before the adsorption of benzene, the magnitude of the effect depending in this case on the temperature of the preliminary adsorption of O_2: with increase of temperature from room temperature to 400°C, the concentration of benzene radical-cations increased by a factor of approximately 15. The adsorption of SO_2^- has the same effect on the yield of benzene radical-cations as the adsorption of oxygen.

Perhaps the most interesting result of this investigation[23] is the observation of the ESR signal of the SO_2^- radical-anion as a result of the adsorption of SO_2 on mordenite after the preliminary adsorption of benzene. A significant increase of the intensity of the benzene radical-cation signal was observed simultaneously with the appearance of the SO_2^- ESR spectrum.

The authors[23] suggest that the oxidation centre of mordenite includes a tricoordinate aluminium ion, the electron-accepting properties of which are enhanced under the influence of O_2 or SO_2 owing to the inductive effect. The negative charge is distributed between the aluminium ion involved in the one-electron transfer and the nearest adsorbed O_2 molecule. Such charge distribution for SO_2 leads to the formation of the SO_2^- radical-anion.

The above mechanism does not of course differ significantly from the mechanism involving the adsorption complex



$$-\left[-O-\overset{\overset{O_2}{\vdots}}{\underset{\underset{O}{|}}{Al}}-O-\right]^{-}-\cdots RH^+,$$

proposed[1] to account for the influence of O_2 on the formation of radical-cations in the adsorption of hydrocarbons on amorphous aluminosilicates. However, this complex can be formed on any aluminosilicate and is not a characteristic feature of mordenites. Nevertheless, as already mentioned above, the radical-cations of benzene and other molecules with high ionisation potentials are formed under normal conditions only on mordenites. We shall consider this process in greater detail below. In conclusion of the analysis of the study of Tokunaga et al.[23], we shall mention here that the ESR spectrum of the SO_2^- radical-anion observed by them is very remarkable. In discussing earlier investigations[2,12], we already noted the fact that, in the ESR study of the radical-cations formed in the adsorption of hydrocarbons on zeolites, it was impossible to detect the unpaired electron captured by the solid. The possible causes of this phenomenon were also briefly discussed, one of them being associated with the delocalisation of the captured electron over the entire bond system of the solid. One cannot rule out the possibility that the appearance of SO_2^- radical-anions observed by Tokunaga et al.[23] is in fact due to the localisation of the captured electron at the sulphur atom.

3. The Oxidising Properties of Mordenites from Which Metal Cations and Aluminium Have Been Eliminated

Few studies on the influence of the elimination of metal cations and aluminium from mordenites on their oxidising and reducing properties are described in the literature. It has been shown[25] that the sharp increase of the ESR signal intensity following the adsorption of anthracene on specimens freed from metal cations is observed for degrees of exchange in excess of 50% (Table 7, Nos. 1–6). The size of the adsorbed molecule is significant in adsorption on mordenites. The dimensions of the small and large elliptical channels in mordenite are 3.8–4.7 Å and 5.8–7.0 Å respectively. The narrow channels (~4 Å) are inaccessible to anthracene molecules. During the metal cation-elimination process, Na^+ ions are removed from the large channels, which increase the effective diameter of the latter[26] and thus the rise of signal intensity may be caused both by the increase in the number of oxidation centres and by the greater accessibility of the bulk of the zeolite to anthracene molecules.

Table 7. Dependence of the number of anthracene radical-ions (N) on the degree of elimination of metal cations and aluminium from mordenite.

No. of specimen	Type of zeolite	SiO_2/Al_2O_3	Degree of exchange of Na^+ for H^+, %	10^{-17} N, spins g^{-1}
1	NaM	10.14	—	no signal
2	»	10.14	15.0	ditto
3	»	10.14	25.0	very weak signal
4	»	10.14	50.0	2.2
5	»	10.14	80.0	7.2
6	HM	10.14	99.4	7.6
7	»	13.3	99.4	10
8	»	16.8	99.4	10
9	»	20.6	99.4	15
10	»	48.0	99.4	4.4
11	»	55.0	99.4	6.7
12	»	73.0	99.4	7.6

The dealumination of an HM specimen is accompanied by an increase in the ESR signal intensity, which reaches a maximum for the preparation with the ratio SiO_2/Al_2O_3 = 20.6. The maximum in catalytic activity observed in a series of investigations for mordenite with this SiO_2/Al_2O_3 ratio[27,28] may be associated with the optimum oxidising properties of this catalyst.

Analysis of the results shows that oxidation centres arise mainly when metal cations are removed from NaM, while dealumination of an HM specimen is accompanied by only a twofold increase of the concentration of these centres.

A detailed study of the oxidising properties of mordenite in relation to the formation of benzene, naphthalene, and anthracene radical-cations has been made[29]. Fig. 8*a* presents the ESR spectrum arising immediately after the adsorption of benzene on an HM zeolite heated in air at 300°C.

The nature of the ESR spectra arising in the adsorption of benzene on an HM zeolite and the influence of O_2 on their appearance, investigated in the above study, confirm the earlier literature data[18,19,22,23]. The HFS constant, equal to 2.3 G, corresponds to the formation of the biphenyl radical. This is confirmed by the presence of 11 HFS components in the adsorption of benzene, i.e. the unpaired electron interacts with 10 equivalent protons. The hypothesis[18] of the formation of a "sandwich" of two benzene molecules appears unlikely, bearing in mind the geometry of the large mordenite channels. Furthermore, in such a model it is not clear which central mordenite lattice cation should be involved in the formation of this "sandwich". The initial activation of the benzene molecule by interaction with an electron-accepting centre and the formation of a charge-transfer complex followed by rapid oxidative dehydrogenation and the formation of a biphenyl radical-cation therefore appear more likely.

Experiments with adsorption of C_6H_5D and 1,4-$C_6H_4D_2$ have shown that there is no preferential abstraction of a D atom in the formation of the biphenyl radical-cation. In fact, if mainly the D atoms were abstracted in the oxidative dehydrogenation, the resulting ESR spectrum would have been identical with that arising in the adsorption of C_6H_6. Examination of Figs. 8 and 9 shows that this is not the case. The spreading of the HFS and the narrowing of the ESR spectrum observed in the adsorption of deuterated benzenes are characteristic of radical-cations in which some of the hydrogen atoms have been replaced by deuterium atoms[30].

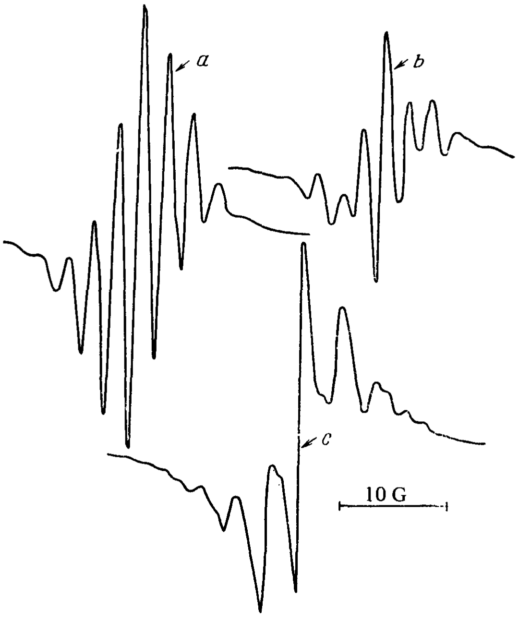


Figure 8. The ESR spectrum of the radical-cations of benzene adsorbed on H-mordenite heated in air at 300°C: *a*) immediately after adsorption; *b*) after 1.5 h; *c*) after 24 h [*a*) and *b*) identical amplification; *c*) amplification greater than in cases *a* and *b*][29].

A characteristic feature of the ESR spectra of adsorbed C_6H_6 is their rapid time variation (Fig. 8), particularly on heating the zeolite. This is associated with the subsequent occurrence of processes leading to the formation of polyphenylene radicals, giving rise to a singlet ESR line. In contrast to C_6H_6, the adsorption of naphthalene and anthracene on an HM zeolite is accompanied by the appearance of much more stable radical-cations, the ESR signals of which (Fig. 10) hardly vary at room temperature over a long period (1 month in the case of anthracene). The different stabilities of the benzene, anthracene and naphthalene radical-cations can probably be explained by the greater reactivity of the biphenyl radicals, leading to the formation of polyphenylenes.

In all the studies on the ESR spectra of molecules with cojugated bonds adsorbed on type X and Y zeolites made hitherto, the adsorbents were subjected to a rigorous preliminary heat treatment (at about 500°C), since it was assumed that centres capable of the formation of radical-cations arise only under these conditions. Fig. 11 illustrates the changes in the concentration of the anthracene, naphthalene, and benzene radical-cations as a function of the temperature of the heat treatment of the HM zeolite in air[29]. Evidently the lower the ionisation potential of the hydrocarbon, the lower the temperature of the heat treatment after which the ESR spectrum of the radical-cation appears. An intense signal of the anthracene radical-cations appears at a heat-treatment temperature as low as ~150°C, although this temperature is too low even for the elimination of the entire molecular water from the mordenite channels. Thus, powerful oxidation centres appear in H-mordenite even at low dehydration temperatures.

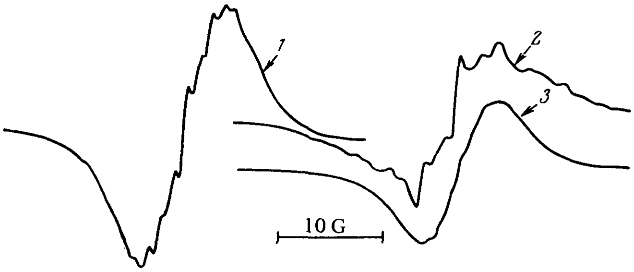


Figure 9. The ESR spectra of deuterated benzenes adsorbed on H-mordenite heated in air at 450°C: 1) immediately after adsorption of C_6H_5D; 2) 24 h after adsorption of C_6H_5D; 3) immediately after adsorption of 1,4-$C_6H_4D_2$ (identical amplification)[29].

One should note that an increase of dehydration temperature entails an increase not only in the number of oxidation centres but probably also in their activity. A dehydration temperature of 150°C is sufficient for the formation of centres capable of oxidising anthracene to the radical-cation, but is insufficient for the appearance of centres on which benzene radical-cations are formed.

The different activities of the oxidation centres suggest that the molecules of aromatic hydrocarbon differing in their ionisation potentials will interact with these centres, forming charge-transfer complexes with different bond strengths. It might therefore have been expected that the anthracene molecule, which has the lowest ionisation potential compared with naphthalene and benzene, would be linked to the electron-accepting centre most strongly and anthracene molecules should therefore displace the radical-cations formed in the adsorption of benzene and naphthalene. It has indeed been found that, when a zeolite with adsorbed naphthalene radical-cations (Fig. 10*a*) is exposed to anthracene in carbon tetrachloride solutions, the spectrum of the naphthalene radical-cations vanishes after 15 min and that of the anthracene radical-cations appears (Fig. 10*b*). It is remarkable that the rate of the displacement process is fairly high, despite the difficulty of the migration of relatively large molecules in the narrow mordenite channels.

One of the fundamental problems in the study of the mechanism of the formation of radical-cations on aluminosilicates and zeolites is that of the nature of the

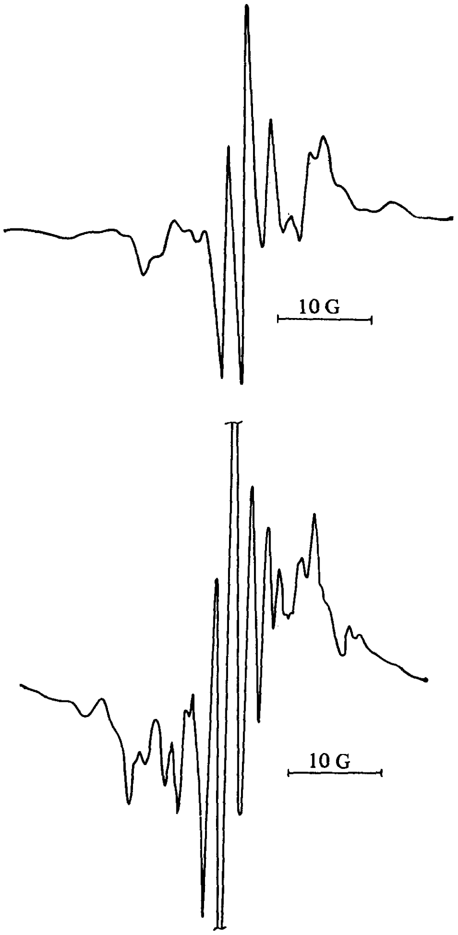
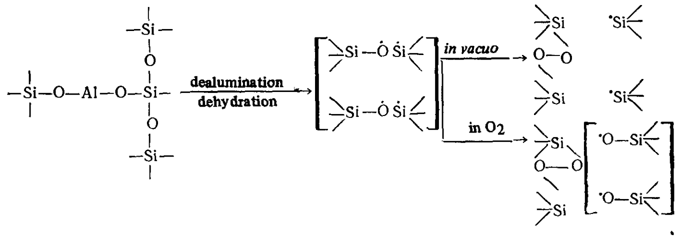


Figure 10. The ESR spectra of the radical-cations of naphthalene (*a*) and anthracene (*b*) adsorbed on H-mordenite[29].

electron-accepting centre and of the role of oxygen. It has been suggested that the electron-accepting centre consists of an Al^{3+} ion. The role of oxygen in the formation of radical-cations, for example in the adsorption of benzene on H-mordenite, reduces to the inductive effect on the Al^{3+} ion, which facilitates the electron transfer[23]. We already noted above that this mechanism does not differ in any significant way from the adsorption complex mechanism proposed[1] to account for the influence of O_2 on the formation of radical-cations in the adsorption of hydrocarbons on amorphous aluminosilicates. It was also emphasised that this mechanism does not explain the appearance of radical-cations in the adsorption of benzenes on H-mordenite, because H-mordenite is the only one of the zeolites investigated hitherto on which benzene radical-cations are formed readily at room temperature without any additional influences on the system, for example ultraviolet irradiation. Consequently the activity of the electron-accepting centres in H-mordenite, at any rate in the formation of benzene radical-cations, should significantly exceed the activity of the electron-accepting centres in other zeolites and amorphous aluminosilicates.

Since treatment of mordenite with oxygen is a necessary condition for the generation of centres responsible for the formation of benzene radical-cations and the mechanisms involving Al^{3+} ions alone does not account for this process, the centres are presumably formed[29] as a result of the interaction of oxygen with silicon. Judging from the intensity of the ESR signal, the number of such centres is small, amounting to approximately one centre for 100 unit cells in anthracene, the number in benzene being smaller by a factor of 2–3.

If it is supposed that dealumination takes place at certain sites in the structure during the formation of mordenite, the subsequent formation of centres can be represented by the following scheme:



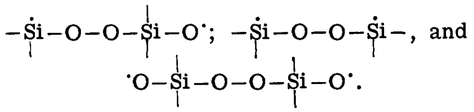
(I)

The pairs of radicals $>$Si–O$^{\cdot}$ and $>$Si$^{\cdot}$ arising in the dehydration process cannot lead to the formation of the Si–O–Si linkage. The point is that there are four different sites in mordenite where Si(Al) atoms are located[31], for which the distance between the nearest Si atoms has been shown by calculations to vary in the range 4.36–5.77 Å. The average Si–O bond length for the same lattice sites varies in the range 1.59–1.63 Å.[31] Consequently the Si–Si distance exceeds by approximately 1 Å twice the Si–O bond length, so that only Si–O–O–Si linkages can formed. On the other hand, the formation of such a peroxy-bridge between two other silicon atoms in the interaction with oxygen is probably impossible owing to steric hindrance.

The $>$Si$^{\cdot}$ centres are relatively unreactive with respect to the adsorption of hydrocarbons, since the unpaired electron is delocalised in these centres over the Si–O bonds. The adsorption of O_2, leading to the formation of Si–O$^{\cdot}$ radicals, thus creates strong electron-accepting centres, active in the formation of radical-cations.

The mechanism described apparently accounts for the appearance of the intense ESR signals in the adsorption of benzene on hydrated H-mordenite heated at low temperatures (Fig. 11). Heat treatment of H-mordenite at low temperatures (~200°C) in the presence of C_2 already gives rise to structure (I), which is active in the formation of benzene radical-cations. Naturally, apart from these centres, the mordenite contains also the usual electron-accepting centres incorporating Al^{3+} ions, which are responsible for the formation of anthracene and naphthalene radical-cations at still lower heat-treatment temperatures (~150°C).

The possibility of the formation of structure (I) is to some extent confirmed by the results of a study by Low[32], who obtained and investigated active silica gels. By methoxylating aerosil with subsequent pyrolysis and heat treatment, he succeeded in obtaining a silica gel which adsorbed considerable amounts of H_2 and O_2. On the basis of adsorption and infrared spectroscopic studies, he postulated[32] the presence on the adsorbent surface of a small number of unusual centres, incorporating silicon atoms, linked by a peroxy-chain:



$-\overset{\bullet}{\underset{|}{\mathrm{Si}}}-O-O-\overset{|}{\underset{|}{\mathrm{Si}}}-O^{\bullet}$; $-\overset{\bullet}{\underset{|}{\mathrm{Si}}}-O-O-\overset{\bullet}{\underset{|}{\mathrm{Si}}}-$, and

$^{\bullet}O-\overset{|}{\underset{|}{\mathrm{Si}}}-O-O-\overset{|}{\underset{|}{\mathrm{Si}}}-O^{\bullet}$.

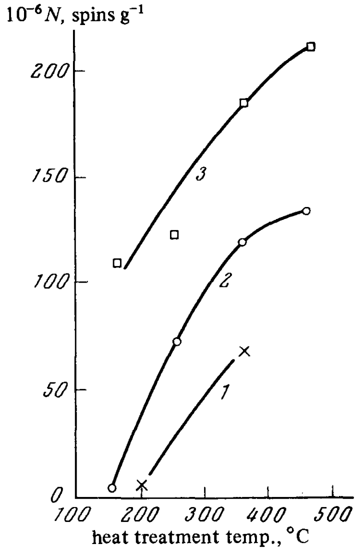


Figure 11. Dependence of the concentration (N) of the radical-cations of benzene (curve *1*), naphthalene (curve *2*), and anthracene (curve *3*) on the temperature of the heat treatment of H-mordenite[29].

Wheareas preliminary methoxylation with subsequent pyrolysis and a fairly severe heat treatment are necessary conditions for the formation of such centres in SiO_2, in mordenite with its unusual crystal structure, centres of this kind can arise under much milder conditions.

IV. CONCLUSION

The studies discussed above have shown that there has been a continuous growth of interest in the study of the oxidising and reducing properties of zeolites. This is due not only to the theoretical importance of the problem but also to its practical aspects, since it has been suggested that the oxidation-reduction centres in aluminosilicate catalysts are involved in the catalytic transformations of hydrocarbons[33].

The characteristic features of the formation of radical-cations on zeolites compared with amorphous aluminosilicates arise from several causes, in particular (1) the specific geometrical structure of zeolites and (2) the presence of more powerful oxidation centres in zeolites. As a result of the latter, radical-cations are formed on zeolites following the adsorption of molecules with high ionisation potentials (benzene and olefins), which is not observed in adsorption on amorphous aluminosilicates.

One of the fundamental problems arising in the study of the oxidation-reduction centres is the elucidation of their nature. The main oxidation centre is believed nowadays to be the tricoordinate Al^{3+} ion (a Lewis centre), but the complete set of data obtained cannot be accounted for solely by the presence of such centres, particularly for H-mordenite. The problem therefore arises whether or not the formation of radical-cations is a specific instance of a general acid–base interaction or whether the oxidation-reduction centres constitute a special group. The elucidation of these problems is of greatest importance for the understanding of the nature of the centres on the surfaces of amorphous and crystalline aluminosilicates and of the mechanism of acid–base catalysis. In this respect, the study of the oxidising and reducing properties of zeolites having a known geometrical structure and susceptible to different types of modification can render invaluable assistance in the solution of the problems formulated above.

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Nuclear Magnetic Resonance Study of Ion-exchange Resin-Solvent Systems

G.S.Bystrov, G.A.Grigor'eva, and N.I.Nikolaev

The results of measurements of NMR spectral parameters (chemical shifts, line widths, and relaxation times) of water molecules, counterions, and adsorbed molecules in the ion-exchange resin phase are discussed in detail and compared and the conclusions concerning their state and motion are analysed. The scope and difficulties in the application of the NMR method to the investigation of ion-exchange equilibria and kinetics are demonstrated.
The bibliography includes 91 references.

CONTENTS

I. INTRODUCTION

Ion-exchange resins are insoluble substances which, however, swell in the solvent and are capable of absorbing from an electrolyte solution positive or negative ions in exchange for equivalent amounts of other ions of like sign[12,13]. The skeleton of synthetic ion exchangers consists of an irregular network of hydrocarbon chains, usually polystyrene chains, connected by a necessary number of cross links. In cation exchangers, fixed groups bearing negative charges ($-SO_3^-$, $-CO_2^-$, $-PO_3^{2-}$, etc.) are grafted to the resin matrix, while in anion exchangers there are similar groups bearing positive charges ($-NH_3^+$, $>NH_2^+$, $>S^+$, etc.).

A dry ion-exchange resin is virtually of no practical interest. All ion-exchange processes, including the dissociation of the ionogenic groups, the diffusion of counterions, and the ion exchange between the external solution and the resin phase take place only in the presence of a solvent. The selectivity of ion exchange is likewise related to the size of the water—exchangeable ion hydrate complex. The electrical conductivity of the ion-exchange resin depends on its water content. In order to optimise ion-exchange processes, it is necessary to investigate the mechanisms of the interaction of all the components in the resin phase. The state of water and of the hydrate complexes in the ion exchanger can be investigated successfully by NMR.

Nuclear magnetic resonance (NMR) yields much information in the study of substances in any state of aggregation. The essential physical features and theory of NMR and the characteristics of the relevant apparatus as well as the results of studies carried out over a period of many years by this method have been described in a number of monographs[1-6] and reviews[7-11]. In the NMR method, the directly measured parameters are the chemical shifts, widths, and integral intensities of the spectral lines and the longitudinal and transverse relaxation times.

More than 10 years have elapsed since the beginning of studies on synthetic ion-exchange resins by nuclear magnetic resonance. However, the wide physicochemical variety of ion-exchange resins, their increasing practical importance, the endeavour to optimise technical exchange processes, and the necessity to investigate the solvent structure within the resins in order to apply the latter as dielectrics or electrolytes are all factors which have now given rise to increased interest in ion-exchange resins. Extensive experimental NMR data on the solvent (usually water) structure in specific types of ion exchangers have accumulated. The parameters of the NMR spectra yield information not only about the state of the external or internal, with respect to the resin, solvent, but also about the state of inorganic or organic exchangeable ions. These parameters usually depend on the initial material of the matrix, the method of preparation of the resin, the nature of the fixed groups and counterions, the percentage content of divinylbenzene (DVB) or another cross-linking agent, the total exchange capacity of the ion exchanger, the shape and size of the resin grains and the proportion of defects they contain, the contamination of the resin, the presence, the concentration and nature of impurity or defect paramagnetic centres in the resin, the content of water or another solvent, and the temperature of the specimen.

II. THE CHEMICAL SHIFT OF INTERNAL WATER PROTONS

1. Characteristics of the Experimental Methods for the Ion-exchange Resin—Water System

The ion-exchange resin—water system consists of swollen resin grains, the space between which may be filled by the solvent. The first NMR study[14] on a suspension of Dowex-50 sulphonic acid cation-exchange resin in water showed that the ^{1}H NMR spectrum of water consists of two lines of approximately equal intensity, belonging to the internal and external water. The chemical shift between the external and internal water may be due to various causes.

It is frequently stated that the structure of internal water is disrupted to a greater extent than that of the external water. This effect[1] must cause a displacement of the line due to the internal water relative to that due to the external water in the direction of higher fields. The displacement of the internal water line can also be caused by the influence of the benzene ring currents on the shielding constant of the nearest protons. It is known[1] that the gradual diluton of a solution with an aromatic solvent leads to an upfield displacement of the proton signal. The major proportion of the signal due to the methyl protons of the solvent in the resin has been attributed to this effect[14]. In the study of the chemical shift in an ion-exchange resin, the influence of aromatic rings on the position of the line is frequently either not considered at all or its contribution is believed to be insignificant.

Another cause of the chemical shift between the water absorbed by the ion-exchange resin and pure water is the difference between the volume magnetic susceptibilities (χ_V) of water and the ion-exchanger material. Gordon[14] estimated χ_V for spherical grains of pure cross-linked polystyrene and, having observed the influence of these grains on the chemical shifts of water, toluene, dioxan, and acetonitrile, concluded that the position of the external solvent line is determined by the effect of volume magnetic susceptibility. For the internal solvent, there is no need[14] to apply a correction for χ_V if the resin grains are ideally spherical. However, it is known[15] that the number of defective grains in the KU-2 and AV-17 resins, most widely used in the USSR, reaches 50–60%. The few available experimental data on the influence of the artificial disruption of resin grains on the ^{1}H NMR chemical shift of water are contradictory. The majority of investigators worked solely with spherical grains or with a small number of defective grains. In subsequent studies, it was shown that the difference between χ_V of water and the swollen resin increases with increase of the degree of cross-linking of the latter, its exchange capacity, and the atomic weight of the counterion. Nevertheless, all workers believe that this difference is small and neglect the correction for this effect; using the rotating tube method, Weiner and Howery[16] determined the absolute values of χ_V in a swollen Dowex-50W cation-exchange resin (with 4, 8, and 12% of divinylbenzene) in 10 ionic forms (H^+, Na^+, NH_4^+, NMe_4^+, Rb^+, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, and La^{3+}). The chemical shifts of the external and internal water relative to a standard were corrected for χ_V taking into account the results. The contribution of the χ_V correction to the chemical shift of the internal water was indeed found to be insignificant.

Since the concentration of the counterions in the resin phase is fairly high, the next factor influencing the position of the ^{1}H NMR line of the internal water is the polarising action of diamagnetic ions on the water molecules, as happens in electrolyte solutions.

The technology of the preparation of ion-exchange resins is such that the latter contain a large percentage of impurities, including paramagnetic impurities. In salt solutions containing parmagnetic ions, fairly large shifts of the ^{1}H NMR signals are observed[1] due to the contact interaction between the unpaired electrons of the paramagnetic ions and protons. The artificial introduction of a small number of Fe^{3+} or Fe^{2+} ions into the KU-2 cation-exchange resin causes[17] an appreciable shift of the ^{1}H NMR line of the water absorbed by the resin. Information about the state of the paramagnetic impurities obtained by other physical methods is therefore of definite value even when the resin is carefully purified.

The dimensions of industrial ion-exchange resin grains vary between 0.002 and 2.0 mm.[13,18] In addition, the majority of investigators have measured the chemical shift of the ^{1}H NMR line due to the water absorbed by the resin relative to the ^{1}H NMR signal of the external water as a standard. It is therefore important to know how the position of the resonance lines of the external and internal water depends on the particle size. Darickova et al.[19] suggested that all resin grains be divided into three groups in terms of their dimensions. The first group includes resins consisting of large grains for which the external water chemical shift is approximately the same as for pure water, while the chemical shift of the internal water is equal to the shift for the aqueous solution of acid at the equivalent concentration. The second and third groups comprise resins with intermediate and fine grains (for sulphonic acid cation-exchange resins, the diameter is less than ~0.1 mm), the decrease of the size of which is accompanied by the mutual approach of the ^{1}H NMR signals of the external and internal water. This phenomenon is explained by an increase of the rate of exchange of water molecules between the resin phase and the external solvent which is confirmed by the dependence of the effect on temperature and the number of cross links. We may add that the average number of hydrogen bonds per molecule in the external water decreases and the effect of volume magnetic susceptibility becomes more pronounced with decrease of the diameter of the resin grains.

It follows from the foregoing that certain causes of the displacement of the ^{1}H NMR resonance lines of an aqueous suspension of an ion exchanger are eliminated in the preparation of the specimen which involves the removal of defective grains and the elimination of paramagnetic and organic impurities from the resin. The presence of impurities in the resin is a cause of the non-reproducibility of the results. Other causes of non-reproducibility may be the non-identity of resins having the same designation but manufactured by different companies and also the different diameters of the resin grains investigated. Small discrepancies may arise in consequence of the differences between the methods used to eliminate the external water (absorption of water by filter paper, centrifugation in tubes with a porous bottom, the passage of a stream of dry air through the column, etc.).

In order to interpret the chemical shift data, it is almost always necessary to have quantitative data for the water content in the resins. It has been shown[20] that there is a satisfactory agreement between the results of the determination of the water content by the Fischer titration method, by the drying method, and from the integral intensities of the ^{1}H NMR signals. However, the titration method is free from the limitations of the drying and ^{1}H NMR methods and yields a rapid and exact estimate of the moisture content (10 wt.% and above) for the majority of resins.

Knowing the water content and capacity of the resin, it is possible to calculate its molality. Reichenberg and Laurenson[21] established that the chemical shift between the lines of the external and internal water is an unambiguous function of the number of water molecules per sulphogroup. Since the chemical shift of the internal water line is proportional[21,22] solely to the molality of the ions in the resin phase, such molality can be determined directly from the chemical shift. However, in a later study[19] it was shown that the concentration of fixed ions can be determined by the ^1H NMR method only for large-grained ion-exchange resins and that the minimum permissible grain size depends on the chemical shift between the internal and external water, i.e. on the degree of cross-linking and molality in the resin phase. According to Darickova et al.[19], the independence of the difference between the chemical shifts of the external and internal water of the resin grain size should serve as a criterion of the possibility of measuring the internal molality in the resin by NMR.

2. Dependence of the Chemical Shift of the Concentration of Counterions

There exist several model representations of ion-exchange resins. The ion exchanger is sometimes[23] compared with a concentrated electrolyte solution, subject to allowance for the characteristics introduced by the resin matrix. ^1H NMR studies on the internal water confirmed[14,24-30] the validity of such comparison. In this case one can use in the interpretation of the chemical shifts in the resin phase certain assumptions and empirical formulae which have been employed previously[9] in the study of aqueous electrolyte solutions by high-resolution NMR. The shift of the ^1H NMR line of the internal water must be mainly determined by the interaction of the water dipoles with the counterions and fixed groups. The molal chemical shifts should reveal positive or negative hydration of the counterion. Here it is necessary to bear in mind that the internal molality in the resin depends on the degree of cross-linking of the latter and the nature of the counterion.

The electrostatic nature of the interaction between water molecules and counterions is expressed by the linear relation between the ^1H NMR signal shift and the square of the reciprocal of the radius of the cation[28] (K^+, Na^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Li^+, and Mg^{2+}) in the KU-2 resin or the corresponding quantity for the anion[29] (F^-, Cl^-, Br^-, and I^-) in the AV-17 resin, the molal chemical shifts in cation exchangers ($\delta^0_{M^+}$) and anion exchangers ($\delta^0_{M^-}$) saturated by univalent and polyvalent counterions are identical as regards sign and order of magnitude[24,25,28,30] with the corresponding values in aqueous solutions of diamagnetic salts. The maximum discrepancy between the resin and solution is observed for H^+ and F^- ions and has been explained by the high capacity of these ions for the formation of ion pairs with the fixed groups.

The consistently lower values of $|\delta^0_\pm|$ in resins for univalent cations[25] and anions[28] compared with the values of $|\delta^0_\pm|$ in the corresponding electrolyte solutions are regarded by the authors as evidence for intensifying ion–ion interactions in the resin. It is emphasised[25,27,28] that the counterions in the resin exhibit their "structure forming" or "structure breaking" properties almost to the same extent as in pure water. The dependences of the ^1H NMR chemical shifts δ of the internal water on the internal molality m† in ion-exchange resins resemble the corresponding plots for aqueous electrolyte solutions and have similar deviations from linearity at high concentrations of the ions in the resin. An exception is the hydrogen-form of the resin, where the linearity persists up to $m = 7$. The values of δ for all the counterions extrapolate to zero when $m \to 0$; thus, the external and internal water have the same chemical shifts at $m = 0$. Since δ tends to zero when $m \to 0$ and does not depend on the grain size, the authors explain the shift of the internal water signal relative to the external water as a result of ion–dipole interactions between the counterions and the solvent.

The deviation from linearity towards decreasing values of $|\delta|$ for the Mg^{2+}-, Be^{2+}-, and Al^{3+}-forms of the cation-exchange resin is more marked than for univalent counterions and begins at lower concentrations. Whereas $|\delta|$ for Be^{2+} and Al^{3+} increases up to 16% DVB under these conditions, albeit at a reduced rate, the plot of $\delta = f(m)$ for Mg^{2+} passes through a maximum and $\delta = 0$ at $m = 3.52$ (which corresponds to 16% DVB). Sharma and Subramanian[27] explain the shape of the $\delta = f(m)$ curve for the Mg^{2+}-form of the cation exchanger by the conversion of the $SO_3^-{-}H_2O{-}Mg^{2+}$ ion pair into the $SO_3^-Mg^{2+}$ contact ion pair (i.e. the fixed group substitutes one water molecule in the first coordination sphere of the counterion). The authors explain the decrease of the overall effect of this cation on the water structure (or on δ for the internal water) by an increase of the number of water molecules outside the first hydration shell. Owing to their high charge density, the Be^{2+} and Al^{3+} counterions retain their first hydration shells in the cation exchanger with 16% DVB. Thus associated species of the type fixed group–solvent–counterion continue to exist and there is only a decrease in the number of molecules outside the first hydration shell. We may add that an increase of the negative shift of the internal water for the Be^{2+}- and Al^{3+}-forms of a sulphonic acid cation-exchange resin with increase of the internal molality is correlated with the capacity of these ions for the protolytic cleavage of the molecules of the water of hydration, as has been pointed out by Zundel[31].

3. Temperature Dependence of the Chemical Shift

(a) The range of positive temperatures. Hydration numbers. Malinowski et al.[32] developed a method for the determination of the total effective hydration numbers of ions h in an electrolyte solution from the temperature dependence of the ^1H NMR chemical shift. Here h is defined as the number of moles of water of hydration per unit molality of the salt. It was assumed that the chemical shift of the water of hydration is independent of concentration and temperature. Since the states of the external and internal water are different in aqueous suspension of an ion-exchange resin, Greekmore and Reilly[33] applied Malinowski's method to the calculation of h in the resin phase using the difference between the temperature dependences of δ_{int} and δ_{ext}. The formula for the calculation of h is

$$h = \frac{55.55}{m}\left[\frac{d\Delta/dt}{d\delta_{H_2O}/dt}\right], \qquad (1)$$

where m is the molality in the resin, $\Delta = \delta_{ext} - \delta_{int}$, and δ_{H_2O}, δ_{ext}, δ_{int} are the chemical shifts of pure water and the external and internal water in an aqueous ion-exchange resin suspension respectively. The Table lists the total effective hydration numbers for different ionic forms of Dowex-AG-50W and KU-2 cation-exchange resins and of Dowex-AG-1 and AV-17 anion-exchange resins taken from a number of communications[27,28,33,34].

A qualitative correlation between the values obtained in the resins and in the corresponding electrolyte solutions

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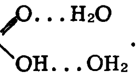
† The molality was altered by changing the degree of cross-linking of the resins.

is evident. The hydration numbers of the counterions in the cation-exchanger phase are systematically lower than the values of *h* for the analogous cations in salt solutions. This fact can be explained by the stronger interaction between the counterion and the fixed group than between the anion and the cation in solution, and also by the more pronounced hydration of anions in solution compared with the fixed groups. It is suggested that one coordination site of a univalent counterion may be occupied by a sulpho-group. The high hydration numbers of bivalent counterions can be explained by the fact that their influence extends to the second hydration shell.

The total effective hydration numbers in different ionic forms of resins.

DVB, wt.%	2	4	8	10	12	16	8—10
			AG-50W[27, 28(33)]				KU-2[34]
NH_4^+	—	2.2	1.7	—	—	1.4	3.5
H^+	0.6	—	2.0 (2.9)	—	—	—	2.7
Li^+	—	—	—	—	—	—	3.7
Na^+	(3.5)	4.8 (3.0)	3.6 (2.9)	—	(2.8)	2.2	3.1
K^+	—	4.4	3.0 (2.7)	—	—	—	3.0
Rb^+	—	3.0	2.6 (2.6)	—	—	1.9	2.6
Cs^+	—	2.7	2.4 (3.2)	—	—	2.1	2.0
Ca^{2+}	—	—	—	—	—	—	4.9
Mg^{2+}	6.4	—	6.4 (6.7)	—	—	7.0	8.0
Zn^{2+}	—	—	—	—	—	—	6.4
Al^{3+}	11.9	—	15.1	—	—	—	
			AG-1[28(33)]				AV-17[34]
OH^-	—	—	—	—	—	—	3.0
ClO_4^-	0.6	0.6	—	0.5	—	—	—
F^-	0.0	1.1	—	1.8	—	—	2.4
Br^-	—	—	(1.3)	—	—	—	1.7
I^-	—	1.6	(1.2)	0.7	—	—	1.4
NO_3^-	—	1.3	—	—	—	—	
Cl^-	—	—	—	—	—	—	1.7

Mank et al.[35] investigated the KB-4P2 carboxylic acid cation-exchange resin in the H^+- and K^+-forms. They obtained $h(H^+) = 2$ and $h(K^+) = 2.9$. They concluded that the water molecules form strong hydrogen bonds with the carboxy-group of the type  $C(=O\ldots H_2O)OH\ldots OH_2$. In the resin containing the K^+ counterion, only some of the COOK groups are dissociated.

The results of measurements of the temperature dependence ($t > 0$°C) of the ^1H NMR chemical shifts of aqueous suspensions of resins with different degrees of cross-linking and in different ionic forms have also been reported in other communications[36-41].

The entire water in the resin can be conveniently divided[12] into free and bound, i.e. the water of hydration. Sharma and Subramanian[28] determined the relative contents of the free and bound water using for this purpose the effective hydration numbers and concluded that the amount of free water for a given content of divinylbenzene is almost constant in resins saturated by alkali metals.

A distinctive feature of a swollen resin compared with an electrolyte solution is that the space between the hydration shells in the resin is "filled" by the hydrophobic matrix. For this reason, *h* can characterise correctly the number of molecules hydrating the fixed group and the counterion, but may not agree with the value of *h* for the corresponding salt solution. An attempt has already been made[28] to relate the hydration numbers to the selectivity of the ion exchanger.

(b) The negative temperature range. Systematic studies by microwave spectroscopy of the state of water in ion-exchange resins in the region of negative temperatures were begun by Nikolaev and coworkers[37,40-42] and then by Mank and coworkers[34,38,39]. As the temperature of an aqueous resin suspension is reduced to zero, the external water crystallises and the intensity of its spectral line becomes negligible owing to its marked broadening as a result of the increasing dipole–dipole interaction of the water protons. The crystallisation of an equivalent Na_2SO_4 solution (1.45 M) or a solution of toluenesulphonic acid takes place[41] at −7° or −30°C respectively. With decrease of temperature below zero, the NMR signals of the internal water protons shift downfield to a greater extent the lower the degree of cross-linking of the resin. This is explained[37,40] by an increase of concentration in the internal solution, which occurs as a result of the freezing out of the "free" water from the resin phase. An interesting experimental result has been obtained[37,40]: for a given ionic form of the resin, there is a definite temperature at which the ^1H NMR chemical shift of the internal water is independent of the amount of cross-linking agent and tends to a limiting value. The latter may be determined by the nature of the counterion. At any rate, the chemical shifts of the internal water in ion exchangers at temperatures below −70°C will be useful for the investigation of stable hydration structures or counterion–water–fixed group complexes.

Mank and coworkers[34,39] noted the possibility of determining the ion hydration numbers from the number of water molecules whose translational motion does not cease below 0°C. By comparing the areas under the experimental ^1H NMR spectral curves at temperatures of aqueous suspensions above and below 0°C, they were able to reach the conclusion that the water which is not bound to the cations crystallises in the resin phase. They found that $h(Ba^{2+}) = 6$ and $h(NH_4^+) = 5$.

The amount of "free" water (not influenced by the counterions and the fixed groups) can be increased sharply by creating artificially large pores within the resin. The states of water in the gel component of the resin and within its pores should differ significantly. However, owing to the rapid proton exchange above 0°C, a single resonance line is observed for the internal water in macroporous cation-exchange resins[41,45]. At −2°C the proton exchange is retarded[37] so much that the line of the internal water in the KU-23 resin splits to give a doublet. A separate ^1H NMR line of the water in the pores is observed down to −15°C and then vanishes owing to its marked broadening, while the signal due to the water in the gel component of the KU-23 resin continues to be recorded down to −70°C. Both lines shift downfield with decrease of temperature.

The study of the state of water in synthetic ion-exchange resins at negative temperatures yields important practical results[37]. The absence of the crystallisation of the internal water gives rise to the hope that ion exchangers with a gel structure are fairly resistant to the action of low temperatures (down to approximately −70°C). On the other hand, the presence of defects and cracks within the resin grains (with a size exceeding 100 Å), in which the phase transition to a crystalline state takes place, leads to the disruption and cracking of resins on cooling. The results obtained for the state of water in the resins on cooling are of interest for the analysis of the changes in the state of water when the temperature is reduced below 0°C in ion-exchange membranes and living cells.

III. THE INTERNAL WATER ^{1}H NMR LINE WIDTH

The width of the ^{1}H NMR spectral lines due to the internal water in synthetic ion-exchange resins depends on a number of factors and is usually appreciably greater than the line width for pure water. In order to interpret the results, it is very important to isolate the dominant cause of the broadening of the line and to exclude the broadening due to preventable effects.

The presence of inorganic paramagnetic impurities in commercial resins leads[14,17] to a significant broadening of the spectral line due to the internal water. Spectrographic studies of the ash of resins, even those which have been carefully washed, reveal[22,43] small amounts of iron and manganese. The paramagnetic centres arising on formation of different defects in the matrix structure, or in the spontaneous scission of sulpho-groups, or as a result of the oxidation of phenolic groups[44] can also be a cause of line broadening.

The line broadening due to the difference between the volume magnetic susceptibilities of water and the resin in spherical grains should not occur[14]. The creation of defects in the grains of the IR-120 sulphonic cation-exchange resin in the H^+-form by a sharp change of temperature[36] or mechanical grinding[22] hardly alters the resonance line width. The opposite result has been obtained[21] for the grinding of a specially prepared sulphonic acid cation-exchange resin to a grain size less than 0.076 mm, the increase in the ^{1}H NMR line width of water following the disruption of the grains depending on the ionic form of the resin. In all the studies where the shape of the grains was stated, spherical resin particles were investigated. However, the effect of volume magnetic susceptibility can be expressed[14] by the influence of the grain size on the line width and can be accounted for by the creation within the grain of inhomogeneous local magnetic fields due to the nearest neighbours. A change in the sulphonic acid cation exchanger grain size (8–15% DVB) by a factor of 2–3 does not alter[21,36] the internal water ^{1}H NMR line width.

Howery and coworkers[16,30] and then Frankel[36] showed by means of various experiments that the main cause of the broadening of the line is the effect of volume magnetic susceptibility.

The internal inhomogeneity of the resin grain (a non-uniform distribution of the cross-links and fixed groups) also leads to an increase of the width of the internal water ^{1}H NMR line, provided that the proton exchange between the chemically non-equivalent equilibrium positions of the water molecules is fairly slow. Otherwise the line width is not a measure of the homogeneity of the resin. This was emphasised by Gordon[14], when he characterised the internal resin grain phase as homogeneous. The fact that resins with very different physical structures (gel and macroporous resins) give comparable line widths[36,37] confirms the occurrence of rapid proton exchange between the inhomogeneous sections of the resin. The existence of a single internal water resonance line, the low rate of proton exchange between the resin grains, and the marked dependence of the position of the internal water line on the counterion molality demonstrate, according to Gordon[14], the narrow limits of the inhomogeneous region between the grains as regards the number of cross-links, the degree of sulphonation, etc. The rate of exchange can be reduced by lowering the temperature of the specimen. Thus the resolution of the ^{1}H NMR signals for water within the macropores and in the gel component of the resin was achieved in the macroporous KU-23 sulphonic acid cation-exchange resin at −2°C.[37] In the range of negative temperature, an appreciable broadening of the internal water resonance line was also observed in gel-type resins[40,42,45].

In certain cases the difference between the line widths for pure water and the water absorbed by the resin may be a result of an incomplete averaging of the dipole–dipole interactions following a decrease of the mobility of the water molecules within the resin grains. The independence of the line width of the degree of cross-linking of the resin[14,36] (the DVB content was varied from 2 to 12%) and of its ionic form[41] ($\Delta\nu \simeq 10$ G for the Cs^+-, K^+-, Na^+-, and Li^+-forms of the KU-2 × 8 cation-exchange resin) shows that, for univalent counterions at temperatures above 0°C, the above cause of the broadening is not dominant. The conversion of the resin into the ionic form saturated by polyvalent counterions leads to a broadening of the internal water line even in highly acidic cation-exchange resins. For example[27], the line widths in the spectra of the Dowex-AG-50W × 16 resin in the Be^{2+}- and Al^{3+}-forms are 72 and 90 G respectively, the line becoming broader with increase of the degree of cross-linking of the resin or with decrease of temperature. This effect has been observed for the Zn^{2+}- and La^{3+}-forms[27] and for the Mg^{2+}-form.[27,33] The dependence of $\Delta\nu$ on the DVB content and temperature has been explained[27,33] by the presence of "free" water and the water of hydration, the large difference between the relaxation times of the two types of water, and the low rate of exchange between their molecules. The narrowing of the line in the spectrum of Dowex-AG-50W × 16 resin in the Mg^{2+}-form may be[27] a result of the formation of a contact ion pair comprising a fixed group and a counterion, i.e. the capture by the SO_3^- group of one coordination site in the first hydration shell of the counterion.

The line widths of the adsorbed water in the spectra of weakly acid and weakly basic resins usually amount to several tens of G, i.e. are much higher than in the spectra of highly acid and highly basic resins[14,22,35,36] and on conversion of the resins into a salt-form the resonance lines are significantly narrowed. The high value $\Delta\nu = 130$ G in the spectrum of the KB-4P2 resin in the H^+-form has been explained[35] by the binding of two water molecules by each COOH group via strong hydrogen bonds. The activation energy for molecular motion $E_a = 4.9$ kcal mole^{-1}, comparable to the dissociation energy of a single hydrogen bond, has been determined[36] from a plot of $\ln(\Delta\nu)^{-1}$ against $1/T$, $\Delta\nu$ being the line width in G and T the absolute temperature. The broadening of the line to $\Delta\nu$ = 30 G in the spectrum of the KU-1 sulphophenol cation-exchange resin is attributed[41] to the influence of the phenoxy-radicals recorded[44] by ESR.

The study of the state of water in synthetic ion exchangers at negative temperatures[38,40–42,45] is of particular interest. In contrast to pure water, the transition to the region of negative temperatures is accompanied by a small increase of the line width, reaching several hundred G at −70°C. The ^{1}H NMR line width for pure ice at −70°C is[41] 65 000 G. If the mechanism of the broadening of the ^{1}H NMR lines of pure water molecules, pure ice, and the water in the resin phase is the same and is associated solely with the mobility of the molecules, then the line width in such systems can be proportional to the correlation time τ_c for the dipole–dipole interaction. Knowing[2] that $\tau_c = 10^{-12}$ s for water, it is possible to estimate the correlation time for ice ($\tau_c \simeq 10^{-7}$ s) and the resin ($\tau_c \simeq 10^{-9}$ s). Thus at -70°C the mobility of the water molecules in the resin is higher by at least two orders of magnitude than in ice, since in reality the ^{1}H NMR line width for the water in the resin can undergo additional broadening owing to the effects discussed above. Mank et al.[45] suggested that the correlation time in an ion exchanger at negative temperatures be determined from the formula

$$\tau_c = A\,\Delta\nu, \tag{2}$$

where $\Delta\nu$ is the line width in G and the constant $A = 1.7 \times 10^{-10}$ G^{-2}. At negative temperature, there is an effect of the degree of cross-linking of the cation-exchange resin[41] and the nature of the counterion[40,45]. The greater the capacity of the cation for hydration the wider the resonance line at a given temperature[45]. Unfortunately the very important experimental data concerning the change in the integral intensity of the ^{1}H NMR signals due to the internal water with decrease of temperature virtually do not exist. Only Mank et al.[39] showed that, on passing from positive to negative temperatures, the number of mobile H_2O molecules per NH_4^+ counterion in the KU-2 cation-exchange resin decreases sharply, from ~12 to ~5, and remains almost unchanged in the range between 0° and -30°C. This effect has been explained[39] by the crystallisation of the free water in the resin.

The dependence of the ^{1}H NMR line width on the internal water content has been investigated in the Dowex-AG-50 (H^+-form; 4, 8, and 16% DVB)[43] and KU-2 (Li^+-form)[46] cation-exchange resins. The marked broadening of the spectral line in the course of the removal of water has been attributed[43] to several causes, the main one of which is the inhomogeneity of the magnetic field in the resin phase. The decrease of the mobility of the water molecules[46] and the structural inhomogeneity of the resin itself[43] can also cause the broadening of the internal water line during the dehydration of the ion exchanger. When the water content corresponds to less than approximately two molecules per counterion, the line width increases without limit[43]. We may recall that, according to Zundel[31], the fixed groups and the hydrogen counterions are associated for this degree of hydration of the sulphonic acid cation exchanger. The sharp increase[46] of the water ^{1}H NMR line in the spectrum of the Li^+-form of the cation exchanger with a moisture content corresponding to approximately 4 H_2O molecules per Li^+ ion has been explained by the stronger sorption of water for low moisture contents in the resin and is also consistent with Zundel's ideas[31]. The diameter of the cavities occupied by water molecules has been estimated[46] from the line width in the spectrum of the fully swollen cation exchanger; it amounts to approximately 8 Å.

A study has been made[45] of the temperature dependence of the line width in the spectrum of the KU-2 cation-exchange resin with different water contents. The decrease of the water content in the Li^+-form of the cation exchanger down to approximately 4 moles of water per equivalent of the resin has little influence on the nature of the $\Delta\nu = f(T)$ curve. This finding confirms yet again that, on passing to negative temperature, only the fraction of the water in the resin which does not form part of the hydration shell of the cations crystallises. The activation energies for molecular motion in the KU-2 resin in the Ca^{2+}-form have been estimated from the slopes of the linear plots of $\ln(\Delta\nu)$ against $1/T$. The values of E_a vary from 16 kcal mole^{-1} for the swollen resin to 8 kcal mole^{-1} for the resin with a water content of approximately one water molecule per Ca^{2+} ion.

Frankel[47] pointed out that additional mechanisms of the broadening of the spectral lines, associated with the existence of concentration profiles in the grains and with a non-uniform distribution of the grains containing different counterions, have been observed in studies on ion-exchange kinetics by ^{1}H NMR.

IV. THE RELAXATION TIMES T_1 and T_2

The system of magnetic nuclei is not isolated, since each nucleus in the molecules is involved in thermal motion and gives rise to a local variable or constant magnetic field at the site of a neighbouring nucleus. The time T_2 is called the spin–spin relaxation time (or the phase memory time) if it yields the average lifetime of a definite spin state due exclusively to a spin–spin interaction. It is frequently called the transverse relaxation time in order to characterise the average lifetime of the spin state, independently of the nature of the interactions bounding it. The time T_1 is called the spin–lattice relaxation time; it represents a measure of the time during which the energy passes from the spin system to other degrees of freedom. In weakly viscous liquids, $T_1 = T_2$, while in solids $T_1 > T_2$.

In an aqueous suspension of Dowex-50W × 8 cation-exchange resin at 31°C,[48] $T_1 = 2.9$ s for the external water and $T_1 = 0.45$ s for the internal water were obtained. The decrease of the internal water relaxation time can be explained by the increase of the correlation time τ_c as a result of the restriction of the mobility of the water molecules by the resin matrix and by the rapid exchange of the excess proton between the water molecules.

Using the nuclear spin echo method, Bleadel et al.[49] investigated the dependence of T_1 and T_2 on the number of water molecules per exchange group (r) in the Dowex-50W cation-exchange resin phase (Na^+-form; 2, 4, 8, and 12% DVB). They observed that, for the same water content in the resin, the times T_1 and T_2 were independent of the degree of cross-linking of the resin with the exception of a small difference in the presence of a high moisture content. This behaviour of the relaxation times may be expected if the internal water molecules are located mainly around the fixed groups and the counterions. In the region where $r > 6$, T_2 hardly varies, while T_1 increases slightly. In the region where $r < 6$, the transverse relaxation time decreases by three orders of magnitude, while the longitudinal relaxation time passes through a minimum near $r = 1.8$ and then increases again. This type of variation of T_1 and T_2 indicates a marked decrease of the mobility of the water molecules in the sulphonic acid cation-exchanger phase following a decrease of the moisture content from six water molecules per Na^+ counterion. The correlation time for the magnetic dipole–dipole interaction for $r = 1.8$ can be estimated from the data of Bleadel et al.[49]: $\tau_c = 4.1 \times 10^{-8}$ s.

T_1 and T_2 for the water protons in the sulphophenol KU-1 cation-exchanger and the sulphonic acid KU-2 cation-exchanger phases (2, 4, 8, and 12% DVB) in the ionic form produced by saturation with alkali metals have also been investigated[50,51] by a pulse method at negative temperatures. The variation of the form of the bifunctional KU-1 cation-exchange resin alters the relaxation parameters of water. An anomalously high ratio T_1/T_2 is observed, which can be explained either by the presence of paramagnetic centres in the KU-1 resin[44] or by the existence of several correlation times. At −25°C, the rate of proton relaxation of water in the KU-2 × 8 resin exceeds by more than an order of magnitude the rate of relaxation of the water protons in a frozen LiCl solution. This finding indicates a larger number of water molecules surrounding the cation–anion pair in the frozen electrolyte solution than is present around the counterion–sulpho-group pair in the resin phase. The increase of the rate of proton relaxation of the internal water with increase of the number of cross-links in a sulphonic acid cation exchanger at −10°C has also been explained by the difference between the water contents. The influence of the type of counterion on the mobility of water molecules in the KU-2 × 8 resin is greatly reduced or masked by other interactions. The increase of the ratio T_1/T_2 with decrease of temperature might be due to the approach of T_1 to its minimum value at the point where $\omega_0\tau_c = 0.6158$. In this case, the correlation time is of a smaller order of magnitude than 10^{-8} s and the activation energy for molecular motion should be estimated from the temperature variation of T_2. The average activation energy for all the forms of the cation exchanger is approximately 9 kcal $mole^{-1}$. The mobility of water molecules in the swollen cation-exchange resin at −50°C is higher than at 25°C in the same cation exchanger, which, however, contains two water molecules less per exchange group, and is much higher than in ice.

Thus the relaxation parameters of the water absorbed by the cation-exchange resin indicate a similarity between the resin phase and the frozen electrolyte solution. The hydrated regions in the resin are surrounded by a virtually immobile matrix while in solutions they are surrounded by ice.

V. MAGNETIC RESONANCE OF THE COUNTERION NUCLEI

Direct information about the state of the hydration shells of the counterions, the intensity of the ion–ion interaction, and the mobility of the counterions can be obtained by studying the NMR parameters of the counterion nuclei in combination with the ^{1}H NMR parameters of the solvent.

1. ^{1}H NMR (nuclear spin $I = 1/2$). ^{1}H NMR can be observed for counterions containing slowly exchanged protons. The ^{1}H NMR spectrum of a suspension of the Dowex-AG-50W × 2 resin in an aqueous $N(CH_3)_4Cl$ solution ($m = 2.5$) contained[14] two lines due to the methyl protons in the counterions present in the resin phase and the cations in the external solution. The ^{1}H NMR line width for the counterions increases with increase of the degree of cross-linking of the resin and approaches smoothly the value corresponding to an aqueous solution of $N(CH_3)_4Cl$. This behaviour of $\Delta\nu$ indicates a decrease of the mobility of the counterions with increase of the degree of cross-linking of the cation exchanger.

The temperature variation of the ^{1}H NMR spectrum of the NH_4^+ counterions in the KU-2 cation-exchange resin has been observed[39]. In the range 20–0°C, the spectrum consists of a triplet due to the spin–spin interaction of the protons with the ^{14}N nucleus. The constant for this interaction is 48 ± 1 G. Above 20°C and below 0°C, the triplet structure signal is converted into a singlet structure.

The ^{1}H NMR spectra of a number of aminoacids absorbed by the Dowex-AG-50W × 4 sulphonic acid cation-exchange resin have been published[52].

2. ^{7}Li NMR ($I = 3/2$). The structural changes near ions whose nuclei have a spin $I > 1/2$ can be studied because these nuclei have an electrical quadrupole moment Q. The nuclei do not possess an electric dipole moment and the energy of the nucleus is therefore independent of its orientation in a homogeneous electric field. However, as a result of the Brownian motion of the species surrounding the resonating nuclei, fluctuations of the electric field gradient arise at the nuclei. In consequence of the presence of Q, an inhomogeneous electric field can induce transitions between the magnetic energy levels, i.e. can create an additional effective magnetic relaxation mechanism. The results of the high-resolution NMR,[53] broad line[54], and spin echo[55] studies published in the first communications demonstrated the likely usefulness of ^{7}Li magnetic resonance in studies on cation-exchange resins.

Mank et al.[46] investigated the dependence of the ^{7}Li NMR chemical shift and line width on the degree of hydration of the sulphonic acid KU-2 cation-exchange resin. The chemical shift of the line due to the counterion nuclei relative to the ^{7}Li NMR signal in an aqueous solution of LiCl is within the limits of the experimental accuracy of the measurement of this quantity when the water content varies from twelve (fully swollen resin) to approximately two water molecules per counterion, i.e. the electron density at the lithium ion remains unchanged. The authors correctly explained the sharp upfield shift of the signal by approximately 16 p.p.m. after the complete dehydration of the resin by the formation of a chemical bond between the counterion and the fixed group, as a result of which the electron density around the lithium nucleus increases.

The breakdown of the structure of the hydration shell of the counterion and the enhancement of the electrostatic ion–ion interaction during the dehydration of the resin must be reflected in the broadening of the ^{7}Li NMR line. A decrease of the degree of dehydration of the resin from the fully hydrated state to approximately four water molecules per counterion is accompanied[46] by a slow increase in the width of the ^{1}H NMR line of the internal water and the NMR line of the lithium counterions. On further dehydration of the resin, the ^{7}Li and ^{1}H NMR line widths increase sharply. Presumably, when the hydration shell of the counterion is strongly deformed after the elimination of even one water molecule from the first coordination sphere, a sulpho-group tends to take its place. This results in an intensification of the ion–ion interaction.

Bystrov and Nikolaev[56,57] showed that the rate of longitudinal relaxation of the lithium counterion nuclei in the KU-2 (or KRS) sulphonic acid cation-exchange resin increases with increase of the molality (i.e. with increase of the number of cross-links in the resin). The activation energies for the relaxation processes E_a were calculated from the temperature variation of T_1 for the lithium counterion nuclei[54]. They decrease in succession with increase of the degree of cross-linking of the resin and are listed below:

DVB, %	soln. LiCl	2	4	8	12
E_a, kcal $mole^{-1}$	4.1	4.2	3.6	3.2	2.3

According to Hertz[58], the activation energy for the reorientation of water molecules in the hydration shell of the Li^+ ion is 4.3 kcal $mole^{-1}$. One may conclude that the modulation of the magnetic and quadrupolar interactions in weakly cross-linked sulphonic acid cation-exchange resins is achieved via the reorientation or jumps of the water molecules in the first hydration shell.

The rate of relaxation of ^{7}Li in an electrolyte solution can be expressed by the sum of several terms:

$$\left(\frac{1}{T_1}\right)_{\rm exp} = \left(\frac{1}{T_1}\right)_{\rm m.d.d.} + \left(\frac{1}{T_1}\right)'_{\rm el.qu.} + \left(\frac{1}{T_1}\right)''_{\rm el.qu.} \cdot \qquad (3)$$

Here the first term characterises the magnetic dipole–dipole relaxation mechanism, which cannot be neglected for the ^{7}Li nucleus[59]. It is proportional to the lifetime of the water molecules in the first hydration shell τ_h^+. The term $(1/T_1)'_{\rm el.qu}$ is determined by the electric field gradient which has arisen as a result of the Brownian motion of the water molecules in the hydration shell of the ion and is characterised either by the reorientation time of the water molecules near the ion τ_r^+ or by τ_h^+. The third term of Eqn.(3) reflects the extent of the direct ion–ion interaction and is proportional to the correlation time τ_{ci}, which characterises the translational diffusion of the ions relative to one another. In the sulphonic acid cation-exchanger phase, the relative values of the terms of the equation may be different from those in solution.

Experiments with light and heavy water showed[57] that at 25°C the ratio of the contributions of the magnetic dipole–dipole and electric quadrupolar relaxation mechanisms to the overall rate of relaxation remain the same as in an electrolyte solution[59]. Thus the times τ_R^+ and τ_r^+ (characterising related motions) increase with the degree of cross-linking of the resin, while the structure of the hydration shell of the lithium counterion (at any rate in cation exchangers with 8% of DVB and less) is deformed insignificantly compared with the hydration shell of the ion in pure water. The changes in τ_r^+ and τ_h^+ during isotope substitution may be neglected[60], while the decrease of the degree of swelling of the cation-exchange resin[61] and the accumulation of residual H_2O in the hydration shells of the counterions[62] on passing from H_2O to D_2O only increase the rate of relaxation of the lithium counterions in D_2O.

The diffusion coefficients of the counterions are known[12,14] to change to a greater extent as the ion-exchange resin structure is altered than those of water molecules. One can therefore expect an increase of the time τ_{ci} with increase of the number of cross links. In order to explain the decrease of E_a on passing from weakly cross-linked to more cross-linked resins, one must suppose that the correlation time τ_{ci} varies with temperature less than do τ_r^+ or τ_h^+. Thus the activation energy characterises different types of motion in each specific case: the Brownian motion of water molecules in the vicinity of the counterion in the KU-2 × 2 cation-exchange resin; the oscillation of the hydrated counterion about the equilibrium position in the KU-2 × 12 resin, where the electric field gradient at the counterion nucleus is a maximum.

In the region of 0°C, the temperature dependence of T_1 undergo[56,57] an abrupt change simultaneously and show a break. This is associated with the displacement of part of the water from the resin on crystallisation of the external water. The sensitivity of the longitudinal relaxation time to structural differences between resins is indicated yet again by the experimental finding that the rate of relaxation of ^{7}Li in a sulphonic acid cation-exchange resin of type KRS (4% DVB) is greater than in the KU-2 sulphonic acid cation exchanger (4% DVB). This apparently reflects the more effective cross-linking in the KRS resin (purified DVB was used) than in KU-2 (industrial DVB was used).

^{13}C NMR ($I = 1/2$). The low abundance of the ^{13}C isotope (approximately 1.1%) and the low relative intensity of the resonance signals (smaller by a factor of approximately 60 than for protons in identical fields) is the main cause of the small number of ^{13}C NMR studies. There has been only one study, by Sternlicht et al.[52], in which a substance (aminoacid) sorbed on the resin (Dowex-AG-50W containing 4 and 8 wt.% DVB) was investigated by ^{13}C NMR. A common feature of the majority of aminoacids is that the ^{13}C line widths for the protonated specimens proved to be only 3–4 times greater than for the deuterated analogues, contrary to the expected increase by a factor of 10–15. Furthermore, $T_1 \gg T_2$ for all measurements and T_2 depends on the degree of cross-linking much more strongly than does T_1. These results can be explained by anisotropic rotations, which persist after the absorption of aminoacid molecules by cation-exchange resins, which leads to a non-zero time-average interaction. It is suggested that internal rotations about one or more intermolecular bonds, for example about the $D_3H^+ \ldots O_2S{-}R$ linkage, may occur in aminoacids. This rotation determines the rate of the spin–lattice relaxation T_1^{-1}. The slow vibrations of the resin matrix determine the rate of the spin–spin relaxation T_2^{-1}. For internal rotation at room temperature, the correlation times are approximately 10^{-9} s, while the vibrations of the ion-exchange resin lattice are described by longer correlation times.

^{19}F NMR ($I = 1/2$). The ^{19}F chemical shifts in the AV-17 anion-exchange resin and KU-2 cation-exchange resin phases have been measured[63] as a function of concentration in the aqueous solutions in which the resins were treated. The amount of adsorbed electrolyte in the resin depends greatly on the concentration in the external solution $c_{\rm HF}$. In a cation or anion exchanger, there is a possibility that the fluorine may exist in the same forms as in aqueous hydrofluoric acid solution, i.e. as cations or the F^- and HF_2^- counterions, as well as HF molecules and associated species $(HF)_n$. However, single ^{19}F resonance lines have been observed in all the systems, which indicates a rapid exchange of fluorine atoms between all the possible states. It has been found that (1) the $\delta = f(c_{\rm HF})$ curve for the KU-2 resin exhibits a positive shift and that for the AV-17 resin a negative shift relative to an aqueous HF solution, (2) in the region where $c_{\rm HF} <$ 5 M, the ^{19}F NMR line for the anion exchanger undergoes a sharp upfield shift, and, in addition, (3) up to the concentration $c_{\rm HF}$ = 18 M the experimental $\delta = f(c_{\rm HF})$ curve for the anion-exchange resin has undergone a downfield displacement relative to the calculated curve. The authors explain the first result by structural differences between anion- and cation-exchange resins, the second result by the existence of several forms of fluorine in the anion-exchange resin, and the third result by the effects of the solvation of the fixed groups by HF molecules. All the results can probably be accounted for by the different proportions of the fluorine species in the anion- and cation-exchange resins.

The chemical shift of the fluoride counterions in the Dowex-1 anion-exchange resin undergoes a downfield displacement[33] with increase of the number of cross links: −0.49 p.p.m. (1% DVB), −0.83 p.p.m. (2% DVB), and −2.24 p.p.m. (8% DVB). The negative ^{19}F NMR shift in anion-exchange resins relative to KF solution can be accounted for by the deshielding of the nucleus of the F^- ion as a result of the formation of an electrostatic linkage between the counterion and the fixed group.

Frankel[47] reported a study of the kinetics of the exchange of F^- and Cl^- counterions in an anion-exchange resin by ^{19}F NMR, but no quantitative interpretation is given.

^{23}Na NMR ($I = 3/2$). It is known that the dominant mechanism of the energy exchange between the spin system and the lattice in electrolyte solutions involves the interaction of the electrical quadrupole moment with the electric field gradient at the site of the nucleus, generated by the neighbouring species. The first term in Eqn.(3) is neglected [T_1(p.p.m.) > 20 s]. The mechanism of the quadrupolar relaxation of the ^{23}Na nuclei in solutions is determined in this case either by the collisions of the hydrate complexes during Brownian motion[64], or by the translational motion of water molecules from the first hydration shell of the ion and back again[64,65], or by a reorientation of the water molecules in the first hydration shell of the ion[58]. Under certain conditions, one of these types of thermal motion may become dominant.

The marked broadening of the resonance line due to the nuclei of the sodium counterions in Dowex-AG-50W × 8 compared with electrolyte solutions was pointed out for the first time by Jardetsky and Wertz[66]; it has been explained by the formation of a strong linkage between the Na^+ ion and the fixed group. The dehydration of the KU-2 cation-exchange resin is also accompanied[54] by a broadening of the resonance line due to the nuclei of the sodium counterions. The line broadening begins when the water content is below approximately 40 wt.%. A molecule of free water is probably removed initially and is followed by molecules from the hydration shell of the counterion. According to Smirnov[54], the dehydration of the cation-exchange resin is manifested much sooner in ^{23}Na NMR than in ^{7}Li NMR. Possibly this reflects the postulated[67] six-molecule hydration shell of the Na^+ ion and the four-molecule shell of the Li^+ ion. In this case one might claim that the individual hydration properties of the Na^+ and Li^+ ions persist also in the cation-exchanger phase. This conclusion was in fact reached by Bystrov and Nikolaev[56], who measured the longitudinal relaxation times T_1 of the sodium and lithium counterions in swollen KRS sulphonic acid cation-exchange resins containing 2 and 4 wt.% DVB and found that at 28°C the ratios of the rates of relaxation of ^{23}Na and ^{7}Li in an aqueous electrolyte solution and in the KRS-2 and KRS-4 cation-exchange resins are respectively 277, 265, and 254, i.e. are virtually constant. If the conclusion[57] concerning the structure of the hydration shell of the lithium counterion is correct, then the hydration shell of the sodium counterion should also not be distorted by, for example, the incorporation of a sulpho-group in the latter.

The hypothesis that one of the four coordination regions around the Na^+ counterion in Dowex-50W is occupied by a sulpho-group was put forward by Greekmore and Reilly[33] on the grounds that the hydration number $h(Na^+) < 4$ (see Table) and that there is broadening of the ^{23}Na NMR line with increase of the degree of cross-linking of the cation-exchange resin. It was concluded that the electrostatic interaction of the counterion with a fixed group is intensified and that the correlation time for the quadrupolar interaction increases with increase of the number of cross links.

However, according to other data[49], obtained in a study of the Dowex-50W cation-exchange resin in the Na^+-form containing 2, 4, 8, and 12% DVB, the relaxation times T_1 and T_2 for ^{23}Na with the same number of water molecules per Na^+ counterion depend strongly on the degree of cross-linking. On the other hand, T_1 and T_2 for the water protons are virtually independent of the number of cross links. When the mechanism of the relaxation of ^{23}Na is considered, the charge density and distribution per unit volume are apparently of considerable importance. During the dehydration of the resin, T_1 and T_2 for the Na^+ counterion nuclei diminish sooner and to a greater extent the lower the degree of cross-linking of the resin. When the water content is less than six water molecules per counterion ($r < 6$), the relaxation times in such resins become comparable and, when $r = 3$, they are virtually equal. This can be explained by the breakdown of the hydration shell as a result of the ion–ion interaction when $r < 6$ and by the formation of a contact ion pair when $r = 3$. The types of variation of the correlation time and of the quadrupolar coupling constant when water is removed from a cation-exchange resin cannot be determined separately.

^{133}Cs NMR ($I = 7/2$). There exist only two preliminary reports of ^{133}Cs NMR studies on cation-exchange resins. The line width for the nuclei of the Cs^+ counterions in the Dowex-AG-50W × 12 sulphonic acid cation-exchange resin has been measured[28] and found to be $\Delta\nu \simeq 500$ Hz. For comparison, we may quote the ^{7}Li NMR line width for the KU-2 sulphonic acid cation-exchange resin (8–10% DVB):[46] $\Delta\nu \simeq 165$ Hz. The longitudinal relaxation times T_1 for the nuclei of the Li^+ and Cs^+ counterions in the bifunctional KU-1 cation-exchange resin are approximately the same[55]: $T_1(^7\text{Li}) \geqslant 10^{-1}$ s and $T_1(^{133}\text{Cs}) \simeq 2 \times 10^{-2}$ s. A rough comparison of $\Delta\nu$ and T_1 shows that, on passing from electrolyte solutions to cation-exchange resins, the rate of relaxation of ^{133}Cs increases more than the rate of relaxation of ^{7}Li. This demonstrates a greater probability of the formation of contact ion pairs of the type $R-SO_3^-{-}Cs^+$.

In conclusion of the section on the magnetic resonance of counterion nuclei, we may mention that the experimental studies described are so far in many respects non-systematic, which greatly hinders comparison of the results. The conclusions reached in the course of the discussion in this Section must therefore be regarded as preliminary. The magnetic resonance of nuclei such as ^{14}N, ^{27}Al, ^{31}P (studies have been made on extraction by organophosphorus compounds; see, for example, Rozen et al.[68]), ^{35}Cl, ^{79}Br or ^{81}Br, ^{85}Rb or ^{87}Rb, ^{127}I, etc. has not been considered at all.

VI. THE STATE OF EQUILIBRIUM OF THE ION-EXCHANGE RESIN–SOLVENT SYSTEM

If the ion-exchange resin remains in contact with the solution for a sufficiently long time, an equilibrium, characterised by a constant ratio of the concentrations of the solute in the resin and in the solution, is established.

1. Determination of the Dissociation Constant

^{1}H NMR studies have been made[69,70] on aqueous solutions of a number of acids (HCl, $HClO_4$, HNO_3, and toluene-*p*-sulphonic acid) over a wide range of concentrations, the chemical shift being used to determine the acid dissociation constant. The observed chemical shift relative to pure water is determined[1] by the fraction of protons present in the hydronium ions (P):

$$\delta_{\text{obs}} = P\,\delta_{H_3O^+},$$
$$P = 3\chi/(2-\varkappa),$$

where χ is the stoichiometric mole fraction of the acid. Dinius et al.[43] investigated Dowex-50 resins with 4, 8, and 12% DVB hydrated to different extents. They postulated that $\delta_{H_3O^+}$ remains approximately constant and compared the relative acid strengths of resins cross-linked to different extents and aqueous acid solutions on the basis of the slopes of the plots of δ_{obs} against P. According to their data, Dowex-50 with 4% DVB, for example, is a stronger acid than HCl or toluene-*p*-sulphonic acid and is comparable in strength to $HClO_4$. The authors point out that the increase of acid strength with decrease of the degree of cross-linking of the resins may be only apparent and may be the result of the different degrees of formation of ion pairs in the resins due to the difference between electrical constants [differing local dielectric constants (Ed. of Translation)]. The method described suffers from a disadvantage—the determination of the position of the line and of P is inaccurate.

Ochiai and Seto[71] used a procedure free from the disadvantage. They investigated a resin fully swollen in water and converted into a mixed form (saturated with hydrogen and metal ions). The resin was kept in solution with specified concentrations of the necessary components and was then separated from it. The concentrations of the components in the resin were inferred from the analysis of the electrolyte composition. The authors[71] obtained the dissociation constant $K = 0.7$. Naturally, the degree of dissociation of the SO_3H group depends on the nature of the second counterion. It was concluded that toluene-*p*-sulphonic acid and the ion-exchange resin are dissociated to approximately the same extent and that the ion exchanger belongs to the category of strong acids.

2. The Adsorption of Solutes

The distribution of the solute between the liquid in the pores and the external solution is frequently referred to as the adsorption of the solute[12].

The adsorption of non-electrolytes. The concentration of the solute in the resin is usually not equal to its concentration in the solution with which the resin is in equilibrium and is characterised by the partition coefficient. The important factors which must be taken into account in the study of non-electrolyte adsorption processes are the sieve effect, the salting-out effects, different kinds of interaction forces, and complex formation processes. The adsorption is also influenced by properties of the resins such as the degree of cross-linking, the matrix structure, and the nature of the ion saturating the resin. The adsorption depends on the properties of the solute—the structure and size of its molecules and its tendency towards complex formation. In addition, the adsorption is influenced by the concentration of the solution and temperature.

Gordon[14] obtained the ^1H NMR spectra of suspensions of anion- or cation-exchange resins in a 5% solution of t-butyl alcohol or an 80% solution of dioxan in water. In the former case, the spectrum of the hydrogen-form of the resin consisted of four lines: two lines due to hydroxyl protons in the resin phase and in solution and two analogous lines due to the methyl protons of the alcohol. The positive shift of the methyl protons of the internal liquid relative to the external solution can be explained mainly by the large diamagnetic anisotropy of the aromatic portions of the matrix due to the circulation of the mobile π-electrons under the influence of the external magnetic field. The effects due to the solvation of the fixed groups and counterions are neglected. In the second case the resonance line of the dioxan protons in the resin phase coincides with the line due to the external dioxan. Gordon concluded from his results that the partition coefficients of the components of the binary solution between the resin phase and the solution can be measured.

Howery et al.[72] investigated the ^1H NMR spectra of suspensions of Dowex-50W × 8 resin (H^+-form) in aqueous solutions of acetone, dioxan, ethyl, isopropyl, and t-butyl alcohols, and dimethyl sulphoxide. The lines due to the internal water were displaced downfield for all the binary mixtures relative to the line of the internal water when the resin was swollen in pure water; the chemical shift of the internal water protons increases with increase of the mole fraction of water in the system. In some cases, selective absorption of the organic solvent by the resin was observed in the presence of a relatively large mole fraction of water. The increase of the chemical shift of the external water with increase of the mole fraction of the organic component in the binary mixture is attributed to the increasing proportion of ruptured hydrogen bonds between water molecules. The opposite effect for the internal water is explained by the polarising action of the cations. Under these conditions, the physical structure of the resin phase consists of hydrated counterions surrounded by molecules of the organic solvent. Apart from preferential hydration, the possibility of a more favourable interaction of the organic molecules with the resin matrix is considered.

The selective absorption of the solvent by weakly basic (Amberlite IR-45) and strongly basic (Amberlite IRA-400) anion-exchange resins in contact with aqueous dimethyl sulphoxide and acetonitrile solutions was investigated by Frankel[73]. Howery et al.[72] analysed the composition of the mixture in contact with the resin, while Frankel[73] removed the external solvent by centrifugation after the attainment of equilibrium in the system and determined by integration of the areas under the spectral lines for the internal liquid. The selectivity coefficient is defined by the expression $K = x_{\text{i}}\bar{x}_{\text{w}}/\bar{x}_{\text{i}}x_{\text{w}}$, where x_{w} and x_{i} are the mole fractions of water and the organic component in the binary solvent and $\bar{x}_{\text{w}}$ and $\bar{x}_{\text{i}}$ are the analogous mole fractions in the resin. It proved to be 3.12 for the fluoride-form of the resin, 1.6 for the chloride-form, 1.4 for the bromide-form, 1.01 for the iodide-form, and 0.7 for the free base. The values of K greater than unity correspond to the preferential adsorption of water. It was concluded that the dominant effects are caused by preferential solvation and the structure of the added solvent and not by the solvation of the fixed groups or steric factors.

Grigor'eva[41] measured the temperature variation of the chemical shifts of the protons of the water and acetone present in the KU-2 × 8 cation-exchange resin in the Rb^+-form. They noted a very interesting experimental fact: the presence of the organic solvent in the external phase leads merely to a decrease of the crystallisation temperature of the external water to −20°C, as happens in mixed solutions[74], while in the resin phase the crystallisation of water is not observed even at −100°C.

Ion-exchange resins in organic solutions. In order to understand the processes involving the selective absorption of one of the components of the binary solution, it is important to know the mechanisms of the interaction of ion-exchange resins with organic solvents of different types.

^1H NMR data for suspensions of the Dowex-AG-50W × 8 cation-exchange resin in dioxan and acetonitrile as well as additional infrared spectroscopic data enabled Gordon[14] to conclude that the equilibrium

$$RSO_3H \cdots X \rightleftarrows RSO_3^- \cdots HX^-$$

in the hydrogen-form of the sulphonic acid cation-exchange resin is displaced to the right when X is dioxan and to the left when X is acetonitrile.

It has been shown[27,75] that the position of the lines due to the hydroxyl and methyl protons of methanol in the ion-exchanger phase is independent of grain size (between 0.297–0.149 and 0.074–0.037 mm), the degree of cross-linking of the resin (between 1 and 8% DVB), and its form (Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Al^{3+} for cation-exchange resins and F^-, Cl^-, Br^-, and I^- for anion-exchange resins). The results can be explained by the formation of contact ion pairs within the resin phase. The maximum chemical shift between the methyl and hydroxyl protons when the cation-exchange resin is in the H^+-form is caused[75] by the displacement of the hydroxyl proton lines towards lower fields due to the proton exchange between the counterions and the OH groups of methanol.

Adsorption of strong electrolytes. When the ion-exchange resin is brought into contact with an electrolyte solution containing ions of the same type as the counterions, there is a possibility of the simultaneous sorption from solutions of ions of both charge types. The amount of adsorbed substance depends on the nature of the solutes, the degree of cross-linking of the resin, the nature and degree of ionisation of the functional groups of the resin, the electrolyte concentration, and a number of other factors.

Dinius and Choppin[76] investigated the distribution of an acid (HCl or $HClO_4$) between an aqueous solution of the acid and the Dowex-50 (4% DVB) sulphonic acid cation-exchange resin and established that the amount of sorbed HCl is smaller than that of $HClO_4$. The difference between the distributions of hydrochloric and perchloric acids is attributed by the authors to the different effects of HCl and $HClO_4$ on the water structure. It has been established by NMR[69] and infrared spectroscopy[77] that the dissolution of $HClO_4$ in water leads to a greater breakdown of the water structure than the dissolution of HCl. In their communication[43], Dinius et al. point out that the water structure in the resin phase is disrupted to a greater extent than in pure water. They therefore suggest that the ions derived from $HClO_4$ are sorbed more readily by the resin than those derived from HCl.

Reichenberg and Laurenson[21] found that the chemical shift of the signal due to hydronium ions from the position of the line for pure water is 11.5 p.p.m., and that the experimental relation $\delta = f(P)$ deviates from linearity with increase of P. Dinius and Choppin[76] also showed that the behaviour of the chemical shift for the internal liquid is very similar to that observed in acid solutions. At moderate acid concentrations, the slope of the $\delta = f(P)$ curves decreases in the sequence (HCl + HR) > ($HClO_4$ + HR) > HR, which is attributed to the decrease of the structure-forming effect in the same sequence. The deviation of the curves from linearity begins much sooner for HCl and only slightly sooner, but much more markedly, for $HClO_4$ than in the corresponding acid solutions. The results have been explained by the earlier association of the HCl ions than the association of the $HClO_4$ ions, and in the latter case there is a possibility that the association of RSO_3H begins sooner, in conformity with the qualitative determination[43] of the acid strengths: $HClO_4 > HSO_3R >$ HCl.

The ion-exchange equilibrium. The NMR spectrum of water in the Dowex-AG-50W sulphonic acid cation-exchange resin–water system, in which the resin exists in the mixed ($H^+ + NH_4^+$)-form, consists[14] of two lines (corresponding to the external and internal liquids). This indicates a rapid proton exchange between the hydration shells of the H^+ and NH_4^+ ions. Howery and coworkers[30,78] investigated by NMR the Dowex-50W (4, 8, and 12% DVB) cation-exchange resin in equilibrium with an aqueous HCl and NaCl solution (the overall molar concentration of cations was 0.02, the ratio of the cations in solution being varied). The proton chemical shift of binary electrolyte mixtures is known[1,79] to be an additive quantity, and to depend on the nature and concentration of each ion separately. It has been found that the position of the line due to the internal water in the cation exchanger in the mixed ($H^+ + Na^+$)-form depends analogously on the ratio of the concentrations of the counterions. The experimental results and the theoretical values calculated assuming additivity of the proton chemical shifts proved to be very similar. Since the moisture content in the resin changes on passing from one form of the latter to another, it has been suggested that the expected chemical shift be calculated, taking this effect into account, by the formula[30]

$$\delta = \frac{\delta_H \bar{x}_H w_H + \delta_{Na} \bar{x}_{Na} w_{Na}}{\bar{x}_H w_H + \bar{x}_{Na} w_{Na}},$$

where δ_H and δ_{Na} are the shifts for the internal water in the cation exchanger in the H^+- and Na^+-forms, $\bar{x}_H$ and $\bar{x}_{Na}$ the equivalent fraction of the H^+ and Na^+ ions in the resin, and w_H and w_{Na} the water contents in the corresponding forms of the resin. Thus each counterion influences the chemical shift of the nearest protons independently of other counterions. This very important conclusion enabled Howery and coworkers[30,78] to regard an ion-exchange resin as a concentrated electrolyte solution. Furthermore, they suggest that the ^1H NMR method be used to determined the equivalent fraction of a specific counterion when the chemical shifts of water in each ionic form of the resin differ by not less than 20 Hz.

VII. EXCHANGE PROCESSES

1. Proton Exchange Between the Resin Phase and the Solution

As already mentioned, the spectrum of a suspension of resin grains in water consists of two lines. For simplicity, we shall assume that all the water protons in the ion-exchange resin phase exist in a single state A and have a resonance frequency ω_A, their lifetime in this state is τ_A, and the population of the state is P_A. The protons of the water filling the space between the grains are in a state B and have the corresponding values of ω_B, τ_B, and P_B, and $P_A + P_B = 1$. If the lifetimes τ_A and τ_B are long compared with $(\omega_A - \omega_B)^{-1}$, then the spectrum consists of two separate signals located in the vicinities of the frequencies ω_A and ω_B (slow exchange). In the other limiting case (rapid exchange), τ_A and τ_B are smaller than $(\omega_A - \omega_B)^{-1}$; the spectrum then consists of a single line centred on $\omega_{av} = P_A\omega_A + P_B\omega_B$. The intermediate cases, frequently encountered in practice, have been discussed in detail in the book by Pople et al.[1] On the basis of the distance between the signals, Gordon[14] established the lower limits (0.004–0.1 s) to the average lifetime of water in any phase. Frankel made a similar estimate for the macroporous Amberlite-200 cation-exchange resin[36]. The rate of exchange of the solvent between the external and internal water is less than 100 s^{-1} for the hydrogen-form and 20 s^{-1} for the sodium-form of the resin. Since individual lines for the water in the pores and in the gel fraction of the resin were not obtained, the rate of proton exchange between these components of the resin must be more than 2×10^3 s^{-1} (at 25°C). Such high rates of exchange in the macroporous cation-exchange resins can be explained by a high surface area.

Dinius et al.[43] used heavy water to determine the lifetime of the protons in a particular phase. The resin grains swollen in H_2O were placed in D_2O (the reverse experiment was also performed). The rate of diffusion was determined from the time variation of the shape of the spectrum, i.e. from the increase of the signal due to the water protons which have diffused from the ion-exchange grain and from the decrease of the signal due to the internal water. For the Dowex-50 × 4 resin (grain size approximately 0.15 mm), the duration of the exchange was 13 s, which corresponded to a diffusion coefficient of 8×10^{-6} cm^2 s^{-1}. Using a similar method, Greekmore and Reilly[48] also found that the exchange was almost completed in 10 s. Using the double resonance method, the authors then found the rate constant for the free exchange of the water protons between the internal and external phases in a suspension of Dowex-50W × 8 resin, the result being $k = 7.3 \times 10^{-1}$ s^{-1}. However, they emphasise that the observed constant characterises only the type of ion exchanger investigated, since it depends on the degree of cross-linking, the grain size, the nature of the counter-ion, etc.

The possibility that the observed rates of proton exchange characterises the exchange of water molecules between the external and internal phases, since the rate of proton exchange is close to the rate of exchange of ^{18}O and the self-diffusion coefficients of water measured by the tracer atom method (^{18}O) and the proton magnetic resonance method are the same, is pointed out in both investigations[43,48].

2. Kinetics of Ion Exchange

Since the chemical shift of the protons of the water in the resin phase depends significantly on the ionic form of the resin, it is natural to employ the ^1H NMR method to follow the transition of the resin from one form to another, i.e. to investigate the kinetics of ion exchange. Attention was already drawn to this factor in an early study by Gordon[14].

Frankel[47] carried out a thorough investigation of the kinetics of the exchange between a mixture of granular resins in two different ionic forms (the exchange of H^+ for Na^+ and NH_4^+). In some of the experiments, the space between the grains was filled with cyclohexane, which facilitated the interpretation of the ^1H NMR spectra, since the signal due to the external water was eliminated. Analysis of the ^1H NMR spectra obtained and the kinetic curves permitted a number of important conclusions: the dependence of the rate of exchange on the square of the grain radius confirmed the internal-diffusion mechanism of exchange. A correlation was noted between the results obtained by the radioisotope method and the NMR method for ion-exchange resins of different types and different degrees of cross-linking: For the successful employment of the NMR method, it is necessary to achieve an effective resolution of the lines of the internal and external water or the lines corresponding to different forms of the resin. In particular, Frankel was unable to follow the kinetics of the exchange between the resins in the F^-- and Cl^--forms owing to the inadequate resolution of their ^1H NMR spectra. The application of the NMR method to the investigation of the kinetics of ion exchange has not been brought to a sufficient level of perfection—the fundamental methodological problem concerning the identity of the observed chemical shifts of the protons and the degree of exchange undergone by resins under dynamic conditions. At the same time, a number of new fundamental possibilities have arisen, for example the possibility of studying diffusion processes in the absence of a Donnan electrolyte in the resin phase or the exchange between the grains in a mixture of resins.

A series of studies undertaken to investigate further ion-exchange resin–solvent systems by the NMR method were published in 1974–1976.[80–90] Kurilenko and coworkers[80,82] have published a general discussion based on their earlier investigations. The nature of the bonds and the mobility of the exchangeable ions H^+, NH_4^+, Li^+, Na^+, Al^{3+}, and F^- in ion-exchange resins with different water contents have been studied by Zubenko and Mank using the NMR method[83]. They concluded that the exchangeable ions and their water of hydration move together both below and above 0°C. According to the results, the rate of the joint migration diminishes below temperatures between −20° and −30°C. They calculated the activation energy for the migration of the exchangeable ions and attempted to determine the type of bonds formed by the counterions with the fixed ionogenic groups and the surrounding water. The authors noted a high mobility of H^+ ions in the dehydrated KU-2 resin.

Studies on water in the KU-2 × 8 resin carried out by Kvlividze and coworkers[84–86] are of undoubted interest. Almost all the studies discussed above were performed on specimens saturated with water to the maximum extent. Measurements have been made[84,85] of the longitudinal (T_1) and transverse (T_2) relaxation times for water in the resin phase at the start of the saturation of the resin with water. The specimens were carefully washed free of paramagnetic impurities[85,86], since the relaxation times of the water protons in the resin phase depend significantly on the content of such impurities (the relaxation times decrease by up to two orders of magnitude in the presence of Mn^{2+} ions in the specimen at a concentration of 1.3×10^{-2} wt.% [86]).

Bukin and Kvlividze[84] showed that water does not crystallise down to 240 K in a specimen of the KU-2 × 8 resin with 23% of water; at 220 K, the signal due to the water protons is much narrower than the matrix signals and, at approximately 200 K, the spectra of the water contain broad and narrow components; only below 160 K do the NMR spectra consist of broad doublets, indicating a rigid fixation of the water molecules and a weak intermolecular interaction. The experimental data on the variation of the relaxation times T_1 and T_2 with the water content have been presented within the framework of the theory of relaxation in a two-phase system[85]. The transverse relaxation in the two phases is due to identical processes. The average correlation time for the rotation of H_2O molecules ($\tau_c \simeq 10^{-8}$ s) and the translational diffusion time ($\tau_d \simeq 10^{-7}$ s) have been determined. These data agree well with the results of Seredin and Nikolaev[91], who obtained $\tau_d = 0.8 \times 10^{-7}$ s in connection with the estimation of the coefficient of self-diffusion of water by measuring the degree of dynamic adsorption in the KU-2 resin in the Cu^{2+}-form. In the range of water contents compared, the NMR line width for the resin is determined mainly by the motion of the sorbed water protons[85].

The magnetic relaxation time of the water protons in a carboxylic acid resin (cross-linked polymethacrylic acid and its sodium and caesium salts) has been investigated by Narebska and Erdmann[81].

There has been a recent growth of interest in NMR studies on ion-exchange resin—non-aqueous solvent systems. Preliminary data have been obtained[89] from NMR studies of the sorption of ammonia by the KU-2 × 8 cation-exchange resins at reduced temperatures. Mank et al.[87] investigated the NMR spectra of the methanol protons in the KU-2 sulphonic acid cation-exchange resins with degrees of cross-linking corresponding to between 4 and 20% DVB. They established that $CH_3OH_2^+$ ions are formed when the adsorbed alcohol molecules interact with the cation exchanger and that their fraction increases with the degree of cross-linking.

The hydration of the KU-2 sulphonic acid cation-exchange resin in equilibrium with sulphuric acid solutions has been investigated[88,90].

Analysis of the results of studies on ion-exchange resin—solvent system by NMR has led to many possibilities in securing valuable and frequently unique information, although many of the research results refer to some extent to specific instances only. Evidently further systematic investigation of ion-exchange resins by NMR is required.

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The Influence of Polar Substituents at Carbon-Carbon Multiple Bonds on the Properties of Linear Unsaturated Compounds

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Data on the influence of polar substituents at multiple bonds on the physicochemical properties of unsaturated molecules are discussed and reviewed primarily in the light of quantitative estimates of the transmission of influence via multiple bonds. The bibliography includes 202 references.

CONTENTS

I. INTRODUCTION

The problem of the influence of polar substituents at multiple carbon–carbon bonds on the properties of linear unsaturated compounds is part of the general problem of the mutual influence of atoms and atomic groups in an organic molecule and is of considerable theoretical and practical interest in connection with the great importance of unsaturated compounds in nature and technology. During recent years, there has been an appreciable growth of interest in the study of the characteristics and mechanism of the influence of substituents at multiple bonds, because the principle of linear free energies (LFE) has been extended to unsaturated compounds and thus a basis has been created for a quantitative estimation of the influence of substituents in terms of correlation equations of the type of the Hammett equation[1-3]. Fairly extensive data have now accumulated on the influence of polar substituents at multiple bonds on the properties of unsaturated molecules and in many cases quantitative estimates of this influence have been made and certain characteristics of the transmission of the influence via multiple bonds have been discovered. Some advances have been achieved also in the elucidation of the nature and mechanism of the transmission of the influence of substituents via multiple carbon–carbon bonds. Although the individual aspects of the problem have been considered in several reviews[4-8], the data as a whole have not been surveyed.

In the present paper an attempt is made to review the information obtained in the last 10–15 years concerning the influence of polar substituents in compounds of the type $X(CH{=}CH)_nY$ and $X(C{\equiv}C)_nY$, primarily in the light of quantitative estimates of the transmission of influences via multiple bonds.

II. GENERAL POSTULATES

The Hammett equation, which is widely used nowadays to estimate the influence of polar substituents in different classes of organic compounds, has the following general form:

$$Q = \rho\sigma, \tag{1}$$

where Q is the molecular property to be correlated, ρ the reaction constant (a measure of the sensitivity of the property Q to the polar effect of the substituent), and σ the substituent constant (a measure of the polar effect of the substituent relative to the hydrogen atom).

The applicability of Eqn. (I) to unsaturated compounds was demonstrated by Jaffe[8] as early as 1953 and has been proved convincingly by Charton and Meislich[9] in 1958 in relation to unsaturated aliphatic compounds.

A quantitative estimate of the influence of polar substituents on the properties of unsaturated compounds obeying the Hammett equation can be achieved in two ways: (1) by comparing the constants ρ obtained in the correlation analysis of identical properties Q determined under identical conditions using the same method for similar series of saturated, ethylenic, or acetylenic compounds, which makes it possible to determine the relative efficiencies of the transmission of polar influences via *cis*- and *trans*-vinyl groups or via ethynyl linkages compared with the corresponding saturated bridges; (2) by calculating the so called transmission factor[1-3], which makes it possible to estimate the degree of attenuation of the influence of the substituent on molecular properties when a multiple bond is interposed between the substituent and the rest of the molecule.

In its initial form, the transmission factor was defined as the ratio of the reaction constants ρ for the given series X–M–Y [X is the variable substituent, Y the fixed part of the molecule, and M the bridge, i.e. $-(CH{=}CH)_n-$ or $-(C{\equiv}C)_n-$] and ρ_0 for a standard (reference) series X–Y:

$$\pi' = \rho/\rho_0. \tag{2}$$

Thus π' shows to what extent the influence of the substituent is weakened when a multiple bond is inserted between X and the remaining part of the molecule Y, i.e. is a measure of the transmission of electronic effects via the bridge M. Apart from π', the transmission factor is sometimes designated in the literature by the symbols Z and τ.

For a quantitative estimation of the influence of substituents, a transmission factor designated by the symbol γ and defined by the ratio[1,7]

$$\gamma_M = \rho_M/\rho_{-C_6H_4-}, \tag{3}$$

is sometimes used. Here ρ_M is the reaction constant for the series X–M–Y, and $\rho_{-C_6H_4-}$ the reaction constant for the p-XC_6H_4Y series.

In this case, the attenuation of the influence of the substituent is estimated relative to the *p*-phenylene group, the electronic conductivity of which is assumed to be unity. Thus γ is a measure of the transmission of electronic effects via the bridge M relative to the *p*-phenylene system. It follows from Eqns. (2) and (3) that

$$\gamma_{-C_6H_4M-} = \pi'_M.$$

The average accuracy of the transmission factors is to within ± 15% (in the range between 1.6 and 33%).[1, 10]

The quantitative estimate of the influence of polar substituents with the aid of transmission factors is fairly general and rigorous. However, this procedure involves a number of difficulties due primarily to the difficulty of selecting a suitable reference series. In order to obtain correct results, it is necessary to maintain the following conditions: (1) The reference series and the series being compared must differ only in the structure of the bridge in the latter. (2) All the members of the selected series must have the same or similar conformations. (3) The properties compared must be of the same type. For example, in the correlation analysis of kinetic data, the mechanisms of the reactions of the reference series and the series being compared must be identical or, in the correlation analysis of ultraviolet spectroscopic data, the maxima analysed must correspond to the same electronic transitions, etc. (4) The properties Q to be correlated must be determined by the same method under strictly identical conditions. These rules must be observed also in those cases where, owing to the absence of a reference series, the polar influence of the substituents is estimated by comparing the values of ρ for analogous saturated and unsaturated series.

It is noteworthy that cases are frequently encountered where the transmission factors are determined by the ratio of the values of ρ for the test series and ρ_0 for incorrectly chosen reference series. For example, in the determination of π' per double bond (π'_{1F}), acetophenones $XC_6H_5COCH_3$ were chosen as the reference series for the series of chalcones $XC_6H_4CH{=}CHCOC_6H_5$ instead of benzophenones $XC_6H_4COC_6H_5$, which should have been selected[11]. In another study[12] π'_{1F} was found from the ratio of the values of ρ for the chalcols $XC_6H_4CH{=}CHCH(OH)C_6H_5$ (test series) and the chalcols $C_6H_5CH{=}CHCH(OH)C_6H_4X$ (reference series) instead of the $XC_6H_4CH(OH)C_6H_5$ series.

In order to reach a conclusion about the nature and mechanism of the transmission of the influence of substituents via multiple bonds, it is necessary to be able to separate the σ and π effects in correlation analysis. The overall polar effect (P) of a substituent at a multiple bond consists of the sum of the σ and π effects:

$$P = I_\sigma + I_\pi + F + M + C,$$

where I_σ (σ-inductive effect), I_π (π-inductive effect), and F (field effect) refer to the σ effects, while M (mesomeric effect) and C (the effect of direct polar conjugation) refer to the π effects.

Unfortunately the problem of the complete separation of the σ and π effects has not been completely solved[1-3,7,13-16]. However, an approach to this problem is available and makes it possible to infer to some extent whether the σ or π effects makes the dominant contribution to the electronic effect of the substituent and hence the nature and mechanism of the influence of the substituent can be deduced.

This approach consists in the employment of the two-parameter Hammett equation in the form proposed by Taft and Lewis[17-19]:

$$Q = \alpha\sigma_I + \beta\sigma_R; \tag{4}$$

where α and β are reaction constants reflecting the sensitivity of the property Q to the inductive and mesomeric effects respectively. The two-parameter equation proposed by Swain and Lupton[20] has a somewhat different significance. In agreement with Dewar and Grisdale[21], these workers assume that, among the σ effects, the main role is due to the field effect F:

$$Q = fF + rR, \tag{5}$$

where F is the field effect constant of the substituent, R its resonance (mesomeric) constant, and f and r are the regression coefficients for F and R respectively.

The contribution of the resonance influence of the substituent to the correlated property Q is expressed in the form

$$P_R = \frac{\beta \cdot 100}{\alpha + \beta} \tag{6}$$

when Eqn. (4) is used and in the form

$$R = \frac{r \cdot 100}{f + r} \tag{7}$$

when Eqn. (5) is used. P_R and R in Eqns. (6) and (7) represent the resonance (mesomeric) contribution (expressed as a percentage) to the overall polar effect P of the substituent X. The main difference between Eqns. (4) and (5) consists in the set of constants employed.

An approximate estimate of the resonance influence of substituents can be obtained in correlation analysis in terms of the usual one-parameter equation [Eqn. (1)] with the substituent constants varied until the optimum correlation is achieved. The values of P_R are zero for σ_I, 25% for σ_M, 40% for σ_n^0, 50% for σ_n, 62% for σ_n^+, 60% for σ_n^-, and 100% for σ_R.

The number of studies which have now been made on the correlation analysis of the properties of series of the type $X(CH{=}CH)_nY$ and $X(C{\equiv}C)_nY$ is fairly large. For certain types of unsaturated compounds, correlation analysis has been used successfully in relation to vibrational spectra[7,10,11,22-48], proton[7,12,49-56] ^{13}C[56] and ^{19}F[57,58] nuclear magnetic resonance, dipole moments[7,27,44,45,59-62], ultraviolet spectra[7,44,45,60,63], mass spectra[7,64-66], basicity and acidity[7,8,11,37,67-86], polarographic reduction[7,44,45,87-94], reaction kinetics[7,44,67,95-115], and finally the electron densities at the oxygen atom (q_0) of certain carbonyl compounds[89,116].

III. GENERAL CHARACTERISTICS OF THE INFLUENCE OF POLAR SUBSTITUENTS ON THE PROPERTIES OF UNSATURATED COMPOUNDS

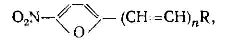
1. Vibrational Spectra

The positions of the characteristic absorption bands in the infrared spectra for a constant substituent Y in compounds of the type $X(CH{=}CH)_nY$ and $X(C{\equiv}C)_nY$ depend primarily on the force constant of the C–Y bond, which is determined by the electron distribution about the bond. It is assumed that infrared spectra are very sensitive to structural changes in the molecule and the method is therefore widely used to investigate the mutual influence of substituents. Carbonyl compounds have been particularly widely investigated among unsaturated compounds, because the stretching vibrations of the carbonyl group are relatively insensitive to the mass of the substituents attached to the carbon atom of the carbonyl group.

Among carbonyl compounds, ketones have been most thoroughly investigated. Thus studies have been made on the infrared spectra of the series $XC_6H_4(CH{=}CH)_n.COCH_3$ [38,41,117,118], $XC_6H_4(CH{=}CH)_nCOC_4H_9$-n [30], and $XC_6H_4(CH{=}CH)_nCOC_4H_9$-t [42] and particularly detailed studies on the series of chalcones and their vinylogues $XC_6H_4(CH{=}CH)_n.COC_6H_4X'$ [10,11,27,29,33,37,40,45,60,119,120] as well as numerous heteroanalogues of chalcones: 1-(2′-furyl)-3-phenylpropenones [29,121], 3-phenyl-1-(2′-thienyl)propenones [24,29], 3-phenyl-1-(2′-pyrrolyl)-propenones [28], 3-phenyl-1-(2′-selenolyl)propenones [34], 3-phenyl-1-(2′-quinolyl)propenones [122], 3-α (or β)-naphthyl-1-(2′-thienyl)propenones [123], etc. as well as the ferrocene analogues of chalcones [32,33]. In addition, there are infrared spectroscopic data for one series of diketones (2-arylideneindan-1,3-diones) [36] and a single series of acetylenic ketones of the type $C_6H_5COC{\equiv}CC_6H_4X$. [46]

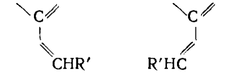
The influence of substituents on the absorption band of the carbonyl group [ν(CO)] in aldehydes has been studied much less, but purely aliphatic aldehydes of the type $X(CH{=}CH)_nCHO$ [43,44,124] and aliphatic-aromatic aldehydes of the series $XC_6H_4(CH{=}CH)_nCHO$ [25,26,42-44,124,125] have been investigated. There have also been several studies on the influence of substituents on ν(CO) for acids and esters in the aliphatic series $X(CH{=}CH)_nCOOR$ (R = H or C_2H_5) and the aliphatic-aromatic series $XC_6H_4(CH{=}CH)_n.COOR$ (R = H or C_2H_5) [9,22,28,35,126]. The influence of substituents on other groups has been studied very little. These investigations are restricted to the XC_6H_4CN, $XC_6H_4CH{=}C(C_6H_5)CN$, and $XC_6H_4CH{=}CHCH{=}C(C_6H_5)CN$ series [31,39,127,128] and there has been a single study of the influence of substituents on the symmetrical and asymmetric vibrations of the nitro-group in the series of ω-substituted α-(5-nitro-2-furyl)polyenes [129].

Table 1 gives a selection of typical examples of the influence of substituents on ν(CO) for some of the series listed above. It shows that the introduction of electron-accepting substituents increases ν(CO) compared with unsubstituted compounds and $\Delta\nu(CO) = \nu(CO)^X - \nu(CO)^H$ decreases with increase of the number of double bonds, Δν(CO) for compounds with 3–4 double bonds hardly exceeding the error of the measurement, which is ± 1–2 cm^{-1} (see Table 1, series 1, 4, and 6). On the other hand, the introduction of electron-donating substituents decreases ν(CO) and a tendency towards a decrease of Δν(CO) down to zero is also observed (Table 1, series 1, 4, and 6). Similar results have been obtained for nitriles [31,39,127,128]. The stretching vibration wave-numbers of the nitro-group in the series of α-(5-nitro-2-furyl)polyenes (series 1) are relatively insensitive to the nature of substituents and an increase in chain length does not affect $\nu(NO_2)^{sym}$:



where R = CHO, $COCH_3$, COOH, COOR′, $CH(OCOCH_3)_2CH{=}NNHCOCH_2CN$, etc. On the other hand, like ν(CO) and ν(CN), $\nu(NO_2)^{asym}$ increases appreciably when the proton is replaced by an electron-accepting group. An increase in chain length in this case also leads to a decrease of $\Delta\nu(NO_2)^{sym}$ down to zero.

Interesting features have been observed in series containing a variable substituent X in the benzene ring. In the first place, the influence of X on ν(CO) is in this case less marked than in aliphatic series (see, for example, series 1 and 2 in Table 1), which can be accounted for by an appreciable weakening of the influence of X during its transmission through the benzene ring. Furthermore, a strong influence of the conformation of the compound on ν(CO) has been noted, in particular ν(CO) for the *cis*-conformers is always smaller than the value for the *trans*-conformers (series 3 and 4 in Table 1). The most interesting feature is that the transition in series 3 and 4 from members of the series with *n* = 0 to members with *n* = 1 is seen to entail an appreciable increase of ν(CO) for the *cis*-conformers, sometimes reaching 10 cm^{-1}, instead of the expected decrease with increase in the length of the conjugation chain. The increase of the rigidity of the C=O bond following its relative approach to the double bond in *S-cis*-conformers can probably be accounted for by the strong interaction of these bonds [131,132]:



S-cis *S-trans*

Table 1. Typical examples of the influence of substituents on the ν(CO) (cm^{-1}) of certain series of unsaturated compounds.

1	2	3	4	5	6	7	8	9	10	11	12
№	Series	*n*	H	CH_3	$CO_2C_2H_5$	NO_2	Cl	OCH_3	$(CH_3)_2N$	Remarks	References
1	$X(CH{=}CH)_nCHO$	0	—	1715	1712				1675	$CHCl_3$	43,44
		1	1730*	1690	1702				1615		
		2	—	1680	1689				1584		
		3	—	1678	1682				1640		
		4	—	—	1681				1681		
2	$X(CH{=}CH)_nCHO$ **	0	1702	—		1712		1687	1668	$CHCl_3$	43,44
		1	1677	—		1685		1675	1655		
		2	1675	—		1680		1675	—		
		3	1675	—		—		—	—		
3	$XC_6H_4(CH{=}CH)_nCOCH_3$	0	1691	—		1700		1683		CCl_4	41,47,118
		1	1697	—		1702		1693		*S-cis*	
		1	1674	—		1681		1670		*S-trans*	
4	$XC_6H_4(CH{=}CH)_nCOC_6H_5$	0	1666	—		—	—	—		CCl_4	33,130
		0	1660	—		—	1656	1654		$CHCl_3$	40,45
		1	1672	—		—	—	—		CCl_4, *S-cis,*	33,130
		1	1653	—		—	—	—		*S-trans*	
		1	1665	—		1670	1666	1660		$CHCl_3$, *S-cis*	40,45
		2	1660	—		1662	1659	1657			
		3	1654	—		1660	1658	1656			
5	$XC_6H_4(CH{=}CH)_nCO_2H$	0	1741			1724			1751	CCl_4	52
		1	1733			1724			1740		
6	$X(CH{=}CH)_nCO_2C_2H_5$***	1	1730*	1724		1735			1685	$CHCl_3$	22
		2	—	1718		1727			1680		
		3	—	1714		1721			1710		
		4	—	1715		1717			1712		
7	$XC_6H_4(CH{=}CH)_nCO_2C_2H_5$	0	1723			1731		1717		CCl_4	35,124
		1	1716			1722		1714			
8	$XC_6H_4(C{\equiv}C)_nCOC_6H_5$	0	1666				1650	1658		CCl_4	46,130
		1	1649			1654	1651	1645			

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*Carbon tetrachloride [124].

**The following values of ν(CO) (in CCl_4) have been published [125] for X = C_6H_5 (the values of *n* are given in brackets): 1710 (0), 1689 (1), 1688 (2), 1685 (3), 1684 (4), and 1683 (5); the values of ν(CO) (CH_2Cl_2) are: 1704 (0), 1679 (1), 1677 (2), 1675 (3), 1674 (4), and 1673 (5,6).

***The following values of ν(CO) (CCl_4) have been published [22] for X = $COOC_2H_5$ (the values of *n* are given in brackets): 1730 (1), 1721 (2), 1715 (3), 1714 (4), and 1713 (5,6).

This feature can probably be used as an additional criterion for the assignment of an α-carbonyl β-unsaturated compound to the *S-cis-* or *S-trans*-form, apart from the usual criteria (the ratio of the intensities of the stretching vibrations of the C=O and C=C bonds and their difference[133]). This means that, when ν(CO) increases after the insertion of a double bond between the carbonyl group and the remainder of the molecule, the isomer obtained belongs to the *S-cis*-series and, when ν(CO) decreases, the isomer belongs to the *S-trans*-series.

In all cases, except for amino-derivatives, the accumulation of double bonds (see series 1 and 8) leads to a decrease of ν(CO). For amino-derivatives, a decrease of ν(CO) is initially observed, but subsequently it increases. The difference between the wavenumbers for adjacent members of the series diminishes and tends to zero.

In relation to the wavenumbers of functional groups or substituents, Eqn. (1) becomes

$$\Delta\nu = \nu - \nu_0 = \rho\sigma, \tag{1a}$$

or

$$\nu = \rho\sigma + \nu_0, \tag{1b}$$

where $\Delta\nu$ is the difference between the wavenumbers for the substituted and unsubstituted members of the series.

A correlation analysis has also been carried out for the intensities A of the vibrational bands, which are functions of the changes in the dipole moments and lengths of the vibrating bonds. The problem of the correlation of A still remains unresolved. Eqn. (1) was used in the following forms:

$$\lg (A/A_0) = \rho\sigma; \tag{1c}$$

$$\Delta A^{1/2} = \rho\sigma; \tag{1d}$$

$$\frac{A^2 - A_0^2}{A_0^2} = \rho\sigma. \tag{1e}$$

It has been noted that the application of Eqns. (1*c*), (1*d*), and (1*e*) frequently yields identical results[39,127,128].

Best results in the correlation analysis of series 1–8 (Table 1) were obtained when the constants σ^+ of σ^0_R were used.

A new correlation equation has been proposed recently[134] for the interpretation of ν(CO) data for aromatic and aliphatic-aromatic carbonyl compounds:

$$\nu(\text{CO}) = 1583 + 38.2\,[X(\text{R}') + X(\text{R}'')]\ (\text{cm}^{-1}), \tag{8}$$

where $X(\text{R}')$ and $X(\text{R}'')$ are constants which depend on the nature of R′ and R″ in the carbonyl compounds R′COR″. The new constants X(R) and the Hammett–Taft substituent constant are linked by the relation

$$\delta' = 0.482\,\sigma^*,\ \delta' = X(\text{R}) - X(\text{CH}_3),\ \text{and}\ \delta = \beta\sigma/10,$$

where $\delta = X(\text{R}) - X(\text{C}_6\text{H}_5)$ and β depends on the type of substituent in the aromatic ring (*para-* or *meta-*) and on the nature of the substituent (electron-donating or electron-accepting). Somewhat later[10,135] Eqn. (1) was extended to unsaturated aliphatic-aromatic compounds of the type RCOCR′ = CR″R‴, the constants X(R) being replaced by new constants X^+(R) (calculated from the electrophilic constants σ^+), which yield an appreciably higher correlation coefficient than the Hammett σ constants. The new constants X^+(R) are empirically related to the σ^+ constants by the equation

$$X^+(\text{R}) = 0.238\,\sigma^+ + 1.077, \tag{9}$$

and when the benzene ring contains more than one substituent, we have

$$X^+(\text{R}) = 0.238\sum_{n=1}^{n} \sigma_i^+ + 0.007n + 1.070.$$

The values of X^+(R) for many substances have been calculated by Eqn. (9) and their applicability to 287 compounds of the type R′CH=CHCOR″ with *meta* and *para*-substituents in the benzene ring has been demonstrated.

It is noteworthy that both Eqns. (1*a*) and (1*b*) and Eqn. (8) with the constants X^+(R) proved to be inapplicable to members of series 4 with n = 2 or 3 (Table 1). This distinguishes series 4 from series 1, 2, and 6, which obey the Hammett equation also for members with n = 2–4.

Table 2. The fundamental wavenumbers (cm^{-1}) in the Raman spectra of the $C_2H_5O_2C(CH{=}CH)_nCO_2C_2H_5$ series (solvent—acetone, exciting light—blue mercury line, ν = 22 938 cm^{-1}).

n	ω_1	ω_2	ω_3	n	ω_1	ω_2
1	1210	1664	1733	5	—	1570
2	1135	1644	1726	6	1142	1562
3	1139	1621	1721	7	1140	1550
4	1139	1596	1717	8	1137	1540

Raman Spectra

Analysis of the Raman spectra of series of polyene esters $C_2H_5O_2C(CH{=}CH)_nCO_2C_2H_5$ (n = 1–8) showed that the vibrational wavenumbers for these compounds change little with increase in chain length[136]. It follows from the data in Table 2 that, with increase of chain length, the addition of each new unit has an increasingly smaller effect on the wavenumbers, i.e. the mutual influence of the atomic groups is weakened.

NMR Spectra

Since chemical shifts characterise the electron density, including the π-electron density, NMR has also found application in the study of the influence of substituents at a multiple bond in unsaturated compounds. The influence of substituents on the chemical shift of olefinic protons has been studied in the *trans*-$CH_3CH{=}CHX$ and *trans*-$C_6H_5CH{=}CHX$ series[49–51], methyl esters of *trans*-α- and *trans*-β-substituted cinnamic acids[50,51], *trans*-β-substituted methyl vinyl ketones and acryloyl chlorides[51], *cis*- and *trans*-cinnamic acids[51–53], chalcols[12,54], substituted styrenes $XC_6H_4CH{=}CH_2$[55], and 1-arylpropynes[56]. Table 3 presents typical examples of the influence of substituents on the chemical shifts of the hydrogen atom in the β-position relative to the substituent. It shows that electron-accepting substituents cause an upfield displacement of the signal due to the proton in the β-position with respect to the substituent, while electron-donating substituents have the opposite effect.

Table 3. Typical examples of the influence of substituents on the chemical shifts δ (p.p.m.) of hydrogen atoms in selected series of unsaturated compounds [solvent—CCl_4, internal standard—tetramethylsilane (TMS)].

$XCH{=}C\underline{H}_2$*[51]

CH_3	H	C_6H_5	Cl	Br	$COOCH_3$	$COCH_3$	CN
4.96	5.33	5.71	5.52	5.88	6.22	6.09	5.91

$XCH{=}C\underline{H}C_6H_5$ [60]

H	Cl	NO_2	CH_3	CHO	COOH	$COOCH_3$	CN	C_6H_5
6.67	6.54	7.92	6.24	7.43	7.72	7.57	7.32	6.99

$XCH{=}C\underline{H}COOCH_3$ [51]

CH_3	H	C_6H_5	Cl	Br	$COOCH_3$	$COCH_3$	COCl
5.76	5.99	6.31	6.16	6.48	6.74	6.57	6.96

p-$XC_6H_4CH{=}C\underline{H}_2$[53,55]

	OCH_3	CH_3	H	Cl	NO_2
cis-	5.07	5.14	5.23	5.28	5.51
trans-	5.61	5.70	5.75	5.81	6.05

p-$XC_6H_4CH{=}C\underline{H}COOH$[53]

	OCH_3	CH_3	H	Cl	NO_2
cis-	5.82	5.92	6.00	6.03	6.31
trans-	6.35	6.47	6.54	6.56	6.74

*The chemical shifts of the underlined hydrogen atoms in the β-position with respect to the substituent are quoted.

Apart from ^1H NMR, the influence of substituents in unsaturated compounds has been investigated by ^{13}C NMR.[56] Table 4 presents the chemical shifts of ^{13}C in the β-position with respect to the aryl group containing the substituent for the series of 1-arylprop-1-enes and 1-arylprop-1-ynes. The introduction of electron-donating substituents causes an upfield shift of the ^{13}C signal, while electron-accepting substituents give rise to a downfield shift.

Table 4. The chemical shifts of the β-^{13}C atoms in the unsaturated group (δ in p.p.m., standard—TMS, no solvent)[56].

Series	X					
	p-CH_3O	p-CH_3	H	m-CH_3O	p-Cl	m-Cl
$XC_6H_4CH{=}\underline{C}HCH_3$	*cis*-125.2	125.9	126.9	—	127.8	—
	trans- 123.6	124.6	125.7	126.1	127.1	—
$XC_6H_4C{\equiv}\underline{C}CH_3$	84.7	85.6	86.4	—	87.7	88.2

Finally, studies have been made[57,58] on the influence of substituents on the chemical shift of the ^{19}F nuclei in $XC_6H_4CH{=}CHC_6H_4F$-p (Table 5). In this case substituents have an appreciable influence on the position of the ^{19}F signal, electron-donating and electron-accepting substituents producing opposite effects on the position of the signal.

A satisfactory correlation has been observed when Eqn. (1) was used in the form

$$\Delta\delta = \delta - \delta_0 = \rho\sigma,$$

where Δδ is the difference between the ^1H, ^{13}C, or ^{19}F chemical shifts for substituted and unsubstituted members of the series.

Table 5. The ^{19}F chemical shifts in $XC_6H_4CH{=}CHC_6H_4F$-p [δ (p.p.m.) relative to 1,1,2,2,3,3,4,4,-octafluorobutane, solvent—benzene].

X	p-OCH_3	H	m-Cl	p-Cl	m-CF_3	m-NO_2	p-NO_2
δ	1.38	0.71	−0.02	−0.17	−0.36	−0.76	−1.35

Dipole Moments

The dipole moment is a direct characteristic of the electronic structure of the molecule. A change in the structure or the introduction of the substituent involves a redistribution of electron density and a change in the dipole moment. In unsaturated compounds, the relative contribution of the conjugation effects is expressed by the mesomeric effect (μ_m), defined as the difference between the dipole moments of the corresponding saturated and unsaturated compounds[137]. With increase in the length of the conjugated system, μ_m also increases[138,139] for all substituents except halogens, whose mesomeric effect is small[140].

Table 6. The dipole moments of certain disubstituted compounds of the type $X(CH{=}CH)_nCHO$ (μ, D; solvent—benzene).[62]

n	1		2		3		4	
X	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}
CH_3	3.49	1.00	3.98	1.49	4.47	1.98	4.95	2.46
$COOC_2H_5$	3.15	1.85	3.19	1.77	3.40	1.98	3.55	1.78
$(CH_5)_2N$	6.24	2.95	7.62	4.33	8.24	4.95	8.50	5.21

The presence at the ends of the conjugated system of substituents of different types (electron-donating and electron-accepting) causes a displacement of electrons from the electron-donating to the electron-accepting groups, which leads to the appearance of an additional dipole moment. The vector difference between the experimental and calculated dipole moments is called the interaction moment (μ_{int}).[141]

It has been shown for a series of substituted benzenes XC_6H_4Y and styrenes $XC_6H_4CH{=}CHY$ that the values of μ_{int} are higher for ethylenic compounds when X and Y are of different electronic types and lower when X and Y are both powerful electron acceptors[142,143]. The same rule holds also for the series of linear polyene aldehydes[62,144]. The insertion of a multiple bond between the substituents in the disubstituted compounds probably promotes the mutual enhancement of conjugation for electron-donating and electron-accepting substituents and weakens the conjugation for two electron-accepting substituents owing to the competitive interaction of the functional groups with the π-electron system of the multiple bonds. The above features of the influence of substituents on the dipole moments of unsaturated compounds are illustrated by examples in Table 6. It is noteworthy that high interaction moments (μ_{int}) are observed for all aliphatic polyenes, the moments increase with chain length in an acceptor–donor system, change little in an acceptor–acceptor system, and increase regularly in a methyl–acceptor system.

A completely different behaviour is observed in systems of the type $XC_6H_4(CH{=}CH)_nCOC_6H_5$ (Table 7). In this case, the dipole moments of compounds with n = 1–3 are very close to those for substituted benzophenones, and the μ_{int} are very low, except for amino-derivatives. The features of chalcones and their vinylogues noted above indicate a weak interaction between the carbonyl group and the π-electron system of the C_6H_4X-p group (except for amino-derivatives). This can be explained both by the appreciable weakening of the influence of the group X owing to the benzene ring and by the non-planar structure of such compounds. X-Ray diffraction and Rayleigh light scattering data for benzophenones[146] and X-ray diffraction analysis of chalcones and their vinylogues[147,148] have shown that the rings are rotated by an angle of 30–31° in benzophenone, 36–37° in p-bromochalcone, 51° in the vinylogue with n = 2, and 3° in the vinylogue with n = 3. Furthermore, the angle between the plane of the ring of p-BrC_6H_4 and the plane of the double bond is 27° in p-bromochalcone, 16° in the vinylogue with n = 2, and 18° in the vinylogues with n = 3. Thus the compounds are non-planar and the transmission of the electronic influence via the mesomeric mechanism should be weakened, i.e. the values of μ_{int} should also be small, which is in fact observed experimentally. The high values of μ_{int} for amino-derivatives can be attributed to the direct polar conjugation between the amino- and carbonyl groups, which presupposes an appreciably smaller (owing to the $=C-C_{Ar}$ bond order) deviation from the planar conformation in the amino-derivative compared with other substituted derivatives.

Table 7. The dipole moments of certain members of the *trans*, *cis*-p-$XC_6H_4(CH{=}CH)_nCOC_6H_5$ series.[45,61,145].

n	0	1		2		3	
X	μ_{exp}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}
H	2.99	3.07	0.11	3.05	0.09	3.39	0.43
NO_2	4.23	4.16	−0.02	4.19	0.01	4.30	0.12
OCH_3	—	3.60	0.28	3.62	0.30	3.61	0.29
Cl	2.95	2.56	−0.33	2.58	−0.31	2.59	−0.30
$(CH_3)_2N$	—	5.22	2.66	5.44	1.88	—	—

The applicability of the Hammett equation in form (1) to the correlation of the dipole moments of non-aromatic unsaturated compounds was first demonstrated by Charton[59]. The optimum correlation is achieved using the constants σ_R^+ for electron-donating substituents and σ_R^- for electron-accepting substituents. Apart from Eqn. (1) in the form

$$\Delta\mu=\rho\sigma,$$

use is made of Eqn. (1*f*) (where account is taken of the distances d^X and d^H between the centres of the substituent Y and the variable substituent X or H at the ends of the unsaturated chain), which was proposed by Exner[149] on the basis of the analysis of numerous dipole moments of aromatic compounds:

$$\frac{\mu^X-\mu^H}{d^X-d^H}=\rho\sigma. \tag{1f}$$

Ultraviolet Spectra

The characteristics of the electronic structures of linear conjugated molecules are manifested most clearly in the ultraviolet absorption spectra. It has been established that the introduction of each new double bond causes a shift of the absorption bands in the spectra of series of disubstituted unbranched polyenes[150–165] towards the visible part of the spectrum, the shift diminishing with increase of the number of double bonds. The dependence of the wavelength of the main absorption maximum on the number of double bonds in the molecule is expressed fairly satisfactorily by the semi-empirical equation of Lewis and Calvin[166]:

$$\lambda^2_{max}=kn.$$

Examples are quoted in a number of communications[123,154,157–159,167–169].

Table 8. The principal absorption maxima in the spectra of certain linear polyenes (λ, nm).

(a) $X(CH{=}CH)_nY$

X	Y	Solvent	n				
			1	2	3	4	5
H	H	Hexane	—	—	274,5[156]	310[156]	341[156]
CH_3	CH_3	»	—	227[167]	267,5[156]	304[156]	334[156]
CH_3	$COOC_2H_5$	Alcohol	206[160]	258[160]	301[160]	334[160]	365[160]
NO_2	$COOC_2H_5$	»	222[160]	281[160]	327[160]	363[160]	—
$(CH_3)_2N$	$COOC_2H_5$	Chloroform	283[182]	345[182]	400[182]	430[182]	—
$COOC_2H_5$	$COOC_2H_5$	Alcohol	210[160]	264[160]	303[160]	335[160]	365[160]

(b) $XC_6H_4(CH{=}CH)_nCOC_6H_5$ (in toluene) (Ref.45)

n	X					
	H	CH_3O	$(CH_3)_2N$	Cl	Br	NO_2
1	311	342	407	317	319	318
2	345	369	435	347	347	358
3	370	400	—	370	372	383

(c) $XC_6H_4(CH{=}CH)_nCOH$ (in alcohol) (Ref.44)

n	X					
	H	CH_3O	$(CH_3)_2N$	Cl	Br	NO_2
0	247	277	339	258	264	263
1	288	323	389	299	302	303
2	330	353	—	329	333	333
3	361	382	—	—	—	—

The following characteristic features have also been noted for linear disubstituted polyenes. The replacement of an ethyl group in dimethylpolyenes by an electron-accepting or electron-donating substituent causes a bathochromic shift of the main absorption maximum, which increases in the following sequence of substituents: $C_2H_5O < COOC_2H_5 < CHO \leqslant COCH_3 < NO_2$. The replacement of the methyl group in the methylpolyenals $CH_3(CH{=}CH)_nCHO$ or the polyenoic esters $CH_3(CH{=}CH)_nCOOC_2H_5$ by an electron-accepting substituent results in small bathochromic or hypsochromic shifts. The replacement of the methyl group by an electron-donating group leads to significant bathochromic shifts (see Table 8, *a*). A similar behaviour has also been observed in the $XC_6H_4(CH{=}CH)_nCHO$ and $XC_6H_4(CH{=}CH)_n.COOC_2H_5$ series[63] (Table 8, *b*).

A detailed study of the ultraviolet spectra of chalcones and their vinylogues[40,45,170-173] and also of the hetero-analogues of chalcones and their vinylogues[174-181] showed that an increase in the length of the conjugated chain also leads to a bathochromic shift of the principal absorption maximum, the shift being particularly marked when electron-donating and electro-accepting groups are introduced simultaneously at the opposite ends of the molecules. Regardless of the nature of the substituents, substitution in the *para*-position of the cinnamoyl part of the molecule leads to a bathochromic shift of the absorption maximum, which increases in the sequence $H < Cl{=}Br < NO_2 < OCH_3 < N(CH_3)_2$ (Table 8).

The correlation of the ultraviolet spectroscopic data leads to satisfactory results when the σ^+ constants are used in Eqn. (1) in the form

$$\frac{1}{\lambda_H} - \frac{1}{\lambda_X} = \rho\sigma.$$

Mass Spectrometry

The possibility of the correlation of the ionisation potentials with the Hammet σ constants when the two-parameter Eqn. (4) is used for substituted ethylenes and unsaturated carbonyl compounds was observed by Charton[7,64]. On the other hand, the correlation between the relative intensity of the common ion peak and the Hammett σ constants in terms of the simple Eqn. (1) in the form

$$\lg Z/Z_0 = \rho\sigma,$$

where Z and Z_0 are respectively the relative intensities of the peaks of the common fragment ion peaks in substituted and unsubstituted compounds, was established by Bursey and McLafferty[183] in relation to benzophenones (with a common benzoyl ion) and was later extended to chalcones and their vinylogues[45,65,66]. An excellent correlation was achieved using the Hammett σ constants for the entire $C_6H_5CO(CH{=}CH)_nC_6H_4X$ series (where $n = 1{-}3$).

The mass-spectrometric method has a number of advantages compared with methods based on measurements in solutions, where it is extremely difficult to take into account quantitatively the interactions between the solvent and solute (the solvation and steric interactions), which distorts the results obtained. Fragmentation in the mass-spectrometer takes place in the gas phase at pressures guaranteeing the absence of collisions of molecules with one another. Thus the use of the mass-spectrometric method makes it possible to determine the exact quantitative characteristics of the efficiency of the transmission of electronic influences by various bridge systems.

Basicity and Acidity

The influence of substituents on the basicity and acidity of unsaturated compounds has been investigated in fair detail. Particularly systematic studies have been made on chalcones and their analogues. Investigation of the comparative basicities of chalcones by the measurements of the shift of the stretching vibration wavenumber of the hydroxy-group in phenols [ν(OH)] in carbon tetrachloride in the presence of chalcones owing to the formation of an intermolecular hydrogen bond[11,79] showed that the introduction of electron-donating substituents [CH_3, CH_3O, and $(CH_3)_2N$] increases the basicity of chalcones [increases $\Delta\nu$(OH)], while the introduction of electron-accepting substituents lowers their basicity [decreases $\Delta\nu$(OH)]. The constants K_{ass} for the association of phenol with chalcones have also been determined from the change in the intensity of the stretching vibration band of the phenolic OH group in the presence of chalcones[82]. As a result, it has been established that K_{ass} increases following the introduction of electron-donating substituents and decreases in the presence of electron-accepting substituents in chalcones.

A dependence of $\Delta\nu$(OH) on the nature of the substituents similar to that noted above has also been observed in the study of the hydrogen bonds between 2,3,4,6-tetrachlorophenol and chalcones[83] and between trifluoroacetic acid and chalcones[84]. In the latter case $\Delta\nu$(OH) is particularly sensitive to the electronic effects of the substituents. The influence of the nature of the substituent on basicity [based on $\Delta\nu$(OH) or the constants K_{ass} for association with phenols] has also been investigated for furan, thiophen, selenophen[79,82-84,184,185], and pyrrole[79,184,185] analogues of chalcones. The same relations as for chalcones have been observed for all the compounds.

Table 9. The values of pK_{BH^+} for certain aminostilbenes and tolanes and the values of pK_a for certain hydroxystilbenes and tolanes.

Series	X			References
	H	H_2N	NO_2	
p-$XC_6H_4CH{=}CHC_6H_4NH_2$-*p* (*trans*-)	3.78	3.95	3.43	76
p-$XC_6H_4C{\equiv}CC_6H_4NH_2$-*p*	3.04	3.18	2.74	77
p-$XC_6H_4CH{=}CHC_6H_4OH$-*p* (*trans*-)	10.73	10.84	10.13	78
p-$XC_6H_4C{\equiv}CC_6H_4OH$-*p*	10.31	10.37*	9.97	78

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*X = OCH_3.

The basicities in certain other series, particularly in amino-[76,77] and hydroxy-derivatives[78] of *trans*-stilbenes and tolanes, have also been determined. Table 9 lists the basicities (in 50% alcohol) of certain compounds. It is seen that a slight but clear influence of the substituents on basicity is observed in this group of compounds too. Electron-donating substituents increase pK_{BH^+} or pK_a, while electron-accepting substituents cause a decrease. The influence of the substituent is more pronounced in the series of stilbenes.

A number of studies have been made on the influence of substituents on the acidity of unsaturated carboxylic acids of the type $XCH{=}CHCOOH$, $RCX{=}CHCOOH$, or $XC{\equiv}CCOOH$[7,8,68-75,80,81,85-87]. Typical examples are compiled in

Table 10. The introduction of electron donors in the β-position of the unsaturated acid lowers its acidity, while electron acceptors increase it.

The majority of the series investigated exhibit a satisfactory correlation with the σ^- and σ^+ constants in terms of Eqn. (1) in the form

$$\lg K/K_0 = \rho\sigma.$$

Table 10. The pK_a values for certain unsaturated acids.

Series	Solvent	X					References
		H	CH_3	COC_6H_5	*n*-OCH_3	*n*-O_2N	
XCH=CHCOOH, *cis-*	80% $CH_3OCH_2CH_2OH$	6.50	7.07	5.33	—	—	87
trans-	ditto	—	6.77	5.78	—	—	87
$XC_6H_4C{\equiv}CCOOH$	50% alcohol	3.40	—	—	3.63	2.87	70

Polarographic Reduction

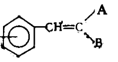
Polarographic reduction constitutes a convenient method for the investigation of the reactivities of unsaturated compounds containing polarographically active groups. The electrochemical reduction of linear polyenals of the type $X(CH{=}CH)_nCHO$ (n = 1–5) and p-$XC_6H_4(CH{=}CH)_nCHO$ (n = 0–3) [7,44,93,125,186] and unsaturated ketones of the type $C_6H_5CO(CH{=}CH)_nC_6H_4X$ (n = 0–3) [45,87,89,90,91,94] has been investigated. It has been noted for both aldehydes and ketones that the accumulation of double bonds facilitates reduction, the increment per double bond decreasing with increase in chain length. Other conditions being equal, electron-accepting substituents facilitate reduction while electron-donating substituents hinder it. As double bonds accumulate, the influence of substituents is abolished (Table 11).

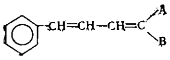
Table 11. The influence of substituents on the half-wave potentials (mV) in selected series of carbonyl compounds (relative to the saturated calomel electrode).

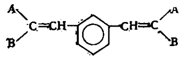
Series	n	CH_3	$(CH_3)_2N$	CN	References
$X(CH{=}CH)_nCHO$	1	1060	*	482	44,93,186
	2	771	1013	518	
	3	598	791	401	
	4	472	646	220	
		H	CH_3O	Cl	
p-$XC_6H_4(CH{=}CH)_nCHO$	0	1007	1068	948	44,93
	1	725	744	628	
	2	507	544	468	
p-$XC_6H_4(CH{=}CH)_nCOC_6H_5$	1	557	584	513	45,94
	2	446	452	428	
	3	354	390	376	

*Not reduced.

Similar relations have been observed for heteroatomic systems [187] of the type







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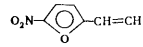
Apart from the investigation of carbonyl compounds, the polarographic method has been used to study the transmission of the polar effect via the furan ring and other bridges, including the vinyl group, in the series of α-nitrofuryl-α'-vinyl derivatives [88,92]:

X=H, CH_3, CHO, COOH, $COCH_3$, $COOCH_3$. 

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There is no unanimous view concerning the interpretation of the dependence of half-wave potentials on the structure of organic compounds [188–191]. Lagutskaya and Dadali [190] believe that the influence of the electronic structure of the substituent and its position in the molecule is reflected in different ways in the electron density at the reaction centre and in the energy levels. They suggest that the free energy of the stage determining the potential of the polarographic process depends primarily on the electron affinity of the molecule and that the influence of substituents on the half-wave potential should be treated from the standpoint of the change in the energy of the lowest vacant molecular orbital. Thus the correlation of the half-wave potentials with the Hammett constants is possible only when there is a direct proportionality between the change in electron density at the reaction centre and the positions of the energy levels, which happens only for a limited range of substituents. Indeed, the correlation between the half-wave potentials and the σ constant is observed solely within narrow series of the same type [44,45].

Eqn. (1) in the form

$$\Delta E_{1/2} = \rho\sigma, \qquad (1g)$$

or the two-parameter Yukawa-Tsuno equation

$$\Delta E_{1/2} = \rho\,(\sigma + r\Delta\sigma_R^+) \qquad (9a)$$

are used for the correlation. In particular, Eqn. (1g) has proved applicable to chalcones using the σ^0 constants and aldehydes of the $R(CH{=}CH)_nCHO$ series using the σ_R^0 constants Eqn. (9a) yielded satisfactory results for the $C_6H_5CO(CH{=}CH)_nC_6H_4X$ (n = 1–3) series.

Reaction Kinetics

The study of the influence of substituents on the reactivity of unsaturated compounds is of particular interest. For this purpose, one can use the influence of substituents on the rate of reaction of a functional group in the $X(CH{=}CH)_nY$ series, where Y is a functional group, or on the rate of addition of an addend to the double bond in the $X(CH{=}CH)_nY$ system, where Y = H or a fixed substituent.

The kinetics of the esterification of unsaturated acids [67,95,101,198] and of the hydrolysis of esters [44,112,192,193] as well as deuterium exchange in monosubstituted acetylenes [99,100,103,194] and in the methyl group of benzylideneacetones [195] have been studied on the widest scale. There are also data for the kinetics of the conversion of benzylideneacetones into oximes [111], the acetylation of aminostilbenes [99] and aminochalcones [110], the formation of complexes of monosubstituted acetylenes with diethylacetamide [108], and also the acid and alkaline cleavage of the $XC_6H_4(C{\equiv}C)_nMR_3$ systems (M = Si or Ge) [96,97,107,197,198]. The influence of substituents on addition to double bonds has been much less investigated. Here one may note studies on the addition of dichlorocarbene to compounds of the type $XC_6H_4(CH{=}CH)_nH$ (n = 1 or 2) [113,115] and the addition of HX in aqueous dioxan to $XC_6H_4C{\equiv}CCOOH$ [106] and of diazomethane to p-$XC_6H_4C{\equiv}CH$. [114]

Table 12. The rates of certain reactions involving the functional group R in the X(CH=CH)$_n$R and X(C≡C)$_n$R systems.

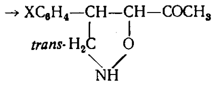
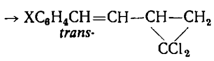
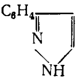
Reaction	Rate characteristic	X					References
1. $XCH{=}CHCOOH + CH_3OH \xrightarrow[35^\circ]{H^+} XCH{=}CHCOOCH_3$ *cis*-isomers *trans*-isomers	10^2k, s^{-1}	H 2.00 —	OCH$_3$ — 4.70	CH$_3$ 3.87 9.07	Cl 3.40 5.13	O$_2$N — 2.62	103
2. $XC_6H_4(CH{=}CH)_nCOOC_2H_5 \xrightarrow{OH^-} XC_6H_4(CH{=}CH)_nCOOH$ (*trans*-isomers) $n=0$ $n=1$ $n=2$ $n=3$	lg k (298° K)	H −2.33 −2.44 −2.60 −2.60	OCH$_3$ −3.02 −2.64 −2.61 −2.60	Cl −0.65 −1.27 −1.83 —	O$_2$N −1.88 −1.94 −2.23 −2.43		44
3. $XC_6H_4C{\equiv}CCOOH + (C_6H_5)_2CN_2 \rightarrow XC_6H_4C{\equiv}CCOOCH(C_6H_5)_2$	10^2k, litre mole^{-1} s^{-1}	H 0.53	p-OCH$_3$ 0.56	p-NO$_2$ 0.25			67
4. $XC{\equiv}CCOOC_2H_5 \xrightarrow{OH^-} XC{\equiv}CCOOH$	k, litre mole^{-1} s^{-1}	H 4.68	CH$_3$ 0.568	COOC$_2$H$_5$ 69.0			193
5. $XCH{=}CHCOOC_2H_5 \xrightarrow{OH^-} XCH{=}CHCOOH$ *trans*-isomers	k, litre mole^{-1} s^{-1}	H 0.0779	CH$_3$ 0.013	COOC$_2$H$_5$ 4.47			193
6. $XC{\equiv}CH \xrightarrow[NH_3, D]{KNH_2} XC{\equiv}CD$	k_{rel}	H 1	OCH$_3$ 0.5	CF$_3$ 10 000			99
7. $XC_6H_4CH{=}CHCOCH_3 + NH_2OH \xrightarrow[pH\ 7.6]{}$ $\rightarrow XC_6H_4CH{=}CHC({=}NOH)CH_3$	k, min^{-1}	H 0.5	p-OCH$_3$ 0.45	p-NO$_2$ 2.6			111
8. $XC_6H_4(C{\equiv}C)_nGe(C_2H_5)_3 \xrightarrow[CH_3OH]{HClO_4\ (30^\circ)} XC_6H_4(C{\equiv}C)_nH$ $n=2$ $n=3$	10^3k, min^{-1}	H 110 34.7	p-OCH$_3$ 255 148	p-NO$_2$ 20.7 6.15			107
9. $XC_6H_4(C{\equiv}C)_nSi(C_2H_5)_3 \xrightarrow[30^\circ]{KOH\ (CH_3OH)} XC_6H_4(C{\equiv}C)_nH$ $n=2$ $n=3$	k_{rel}	H 1 1	p-OCH$_3$ 0.55 0.59	p-NO$_2$ 5.54 3.33			198

Table 12 presents typical examples of kinetic data for certain reactions involving functional groups in unsaturated compounds, while Table 13 lists data for the reactions involving double or triple bonds. Depending on the nature of the reaction, the introduction of electron-donating substituents either reduces (Table 12, examples 2, 4, 6, 7, 9) or increases (Table 12, examples 1, 3, and 8) the reaction rate relative to the unsubstituted compound. Electron-accepting substituents act in the opposite direction (the increase of the rate is illustrated by examples 2, 4-7, and 9 in Table 12 and its decrease is illustrated by examples 1, 3, and 8). It is seen from the data in Table 13 that electrophilic reactions are retarded by electron-accepting substituents, while nucleophilic reactions are retarded by electron-donating substituents.

The correlation analysis of kinetic data is carried out using Eqn. (1) in the form

$$\lg K/K_0 = \rho\sigma.$$

Table 13. The rates of addition to multiple bonds (some examples of the influence of substituents).

Reaction	Reagent (reaction conditions)	Rate characteristic	X			References
			H	n-CH$_3$O	n-NO$_2$	
$XC_6H_4CH{=}CHCOCH_3 \rightarrow$ 	NH$_2$OH (90% methanol; pH 7,6; 17,5°)	k, min^{-1}	3.60	2.55	5.40	111
$XC_6H_4CH{=}CHCH{=}CH_2 \rightarrow$ 	: CCl$_2$ (Cl$_3$COOC$_2$H$_5$, CH$_3$ONa, 0°, petroleum ether)	k_{rel}	1	2.08	0.47	115
$XC_6H_4C{\equiv}CH \rightarrow$ 	CH$_2$N$_2$ (ether)	k, litre mole^{-1} s^{-1}	0.099	0.078	3.225	114

IV. THE CHARACTERISTICS AND MECHANISM OF THE TRANSMISSION OF THE INFLUENCE OF POLAR SUBSTITUENTS VIA MULTIPLE BONDS

The quantitative characteristics of the transmission of the influence of substituents via multiple bonds are based on correlation analysis (see Section II) and on the determination of transmission factors. It is noteworthy that, whereas there have been numerous studies on correlation analysis, the transmission factors have been determined in a much smaller number of instances, which is explained mainly by the difficulty of selecting suitable reference series. Table 14 lists the transmission factors for one (π'_{1F}), two ($\pi'_{2F'}$), three ($\pi'_{3F'}$), and four ($\pi'_{4F'}$) double bonds and for one ($\pi'_{1F'}$), two ($\pi'_{2F'}$), and three (π'_{3F}) triple bonds.

Although the total number of series investigated is not as yet very large (21 series) and certain types of compounds have not been studied at all or have been studied inadequately, nevertheless analysis of the data in Table 14 yields information about certain characteristic features of the transmission of influences via multiple bonds. In the first place, the long range of variation of the values of $\pi'_{1F'}$ [from 0.42 (series 9) to 0.87 (series 1)] is probably evidence that π' for the X(CH=CH)$_n$Y systems depends not only on the nature of the bridge [1,199] but also on the nature of the unchanged part of the molecule Y. Thus the values of π'_{1F} found from the correlation analysis of ν(CO) or ν(CN) are 0.74 (series 2), 0.62 (series 6, *S-cis* in CCl$_4$), 0.82 (series 6, *S-trans* in CCl$_4$), 0.64 (series 10), and 0.61 (series 17). It is therefore hardly useful to combine in a single series compounds of different types, as has been done in series 21, which includes all carbonyl compounds regardless of their nature (aldehydes, ketones, carboxylic acids, and their esters and amides).

Table 14. Transmission factors.

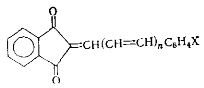
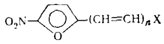
Series	Property	σ	π′	Remarks	Refs
1. $X(CH{=}CH)_nCHO$ *trans-*	μ	σ^+ or σ_R^0	0.87 (1F) 0.68 (2F) 0.56 (3F) 0.43 (4F)		44
»	λ_{max}	σ_R^+	0.85 (1F) 0.75 (2F) 0.62 (3F)		44
»	q_0	σ_R^0	0.47 (1F) 0.22 (2F) 0.10 (3F)		44
2. $XC_6H_4(CH{=}CH)_nCHO$ *trans-*	ν(CO)	σ^+	0.74 (1F) 0.58 (1F) 0.69 (1F)	In CCl_4 In $CHCl_3$ Association of phenol with CO	25, 26 44 199
»	λ_{max}	σ_R^+	0.79 (1F) 0.63 (2F)		44
»	$E_{1/2}$	σ_R^0	0.86 (1F) 0.63 (2F) 0.70 (1F)	50% DMF, pH 2 Abs. DMF, R_4NI	44 199
3. $X'(CH{=}CH)_nCHO$ $X'{=}X, XC_6H_4$, *trans-*	ν(CO)	σ_R^0	0.67 (1F) 0.49 (2F) 0.29 (3F) 0.13 (4F)	$CHCl_3$, CCl_4	44
4. $XC_6H_4(CH{=}CH)_nCOCH_3$ *trans-*	ν(CO)	σ^+	0.47 (1F) 0.54 (1F)	CCl_4, *S-cis* *S-trans*	41
»	Δν(OH..OCR$_2$)	σ	0.76 (1F)		199
»	$E_{1/2}$	σ	0.76 (1F)		199
5. $XC_6H_4(CH{=}CH)_nCOC_4H_9$-t *trans-*	$\Delta\nu_{OH...OCR}$	σ	0.75 (1F)		199
»	$E_{1/2}$	σ	0.73 (1F)		199
6. $XC_6H_4(CH{=}CH)_nCOC_6H_5$	ν_{CO}	σ^+	0.62 (1F) 0.82 (1F) 0.79 (1F) 0.82 (1F)	CCl_4, *S-cis* *S-trans* $CHCl_3$, *S-cis* *S-trans*	11 45
»	ν(OH...OCR$_2$)	σ^+	0.70 (1F)		199
»	ν(OH...OCR$_2$)	σ	0.8 (1F)		78
»	K_{ass}	σ	0.7 (1F)		81
»	μ	σ^+	0.82 (1F)		45
»	$E_{1/2}$	σ^+	0.71 (1F)		199
»	λ_{max}	σ^+	0.72 (1F) 0.55 (2F)		45
»	Z/Z_0	σ	0.72 (1F) 0.25 (2F) 0.11 (3F)		45
7. 	ν(CO)	σ^+	0.72 (1F) 0.76 (1F)	sym. asym.	36 »
8. $XC_6H_4(C{\equiv}C)_nCOC_6H_5$	ν(CO)	σ^+	0.58 (1F)		41
9. $XC_6H_4(CH{=}CH)_nCOOH$ *trans-*	pK_a	σ	0.47 (1F)		8
»	*k*	σ	0.44 (1F)	Esterification	71
10. $X(CH{=}CH)_nCOOC_2H_5$ *trans-*	ν(CO)	σ^+	0.64 (1F) 0.42 (2F) 0.25 (3F)		22 » »
11. $XC_6H_4(CH{=}CH)_nCOOC_2H_5$ *trans-* *cis-* *trans-*	*k*	σ^+	0.52 (1F) 0.33 (2F) 0.13 (3F) 0.43 (1F) 0.50 (1F) 0.54 (1F)	Alkaline hydrolysis, 66% dioxan Ditto, 50% alcohol Ditto » Ditto, 88% alcohol	44 » » 71 » 200

Table 14 (continued).

Series	Property	σ	π′	Remarks	Refs.
12. 	$E_{1/2}$	σ	0.50 (1F) 0.60 (1F)	DMF, R_4NI water, pH 12	92 »
13. $XC_6H_4C{\equiv}CCOOH$	pK_a	σ	0.35 (1F) 0.33 (1F)	85% alcohol 50% alcohol	200 71
»	*k*	σ	0.33 (1F)	Esterification, $(C_6H_5)_2CN_2$	72
14. $XC_6H_4C{\equiv}CCOOC_2H_5$	*k*	σ	0.42 (1F)	Alkaline hydrolysis, 50–88% alcohol	67, 200
15. $Ar(C{\equiv}C)_nHg$	*k*	σ	0.35 (1F)	HCl in dioxan, demercurisation	201
16. $XC_6H_4(C{\equiv}C)_nGe(Ce_2H_5)_3^*$ $n = 0$ $n = 1$ $n = 2$ $n = 3$	*k*	σ	 1 0.66 1.30 0.18	$HClO_4$, degermylation	107
17. $XC_6H_4(CH{=}CH)_nCN$	ν(CN)	σ^+	0.61 (1F) 0.58 (1F)	CCl_4 $CHCl_3$	31, 39, 127
18. $Ar(CH{=}CH)_nH$	*k*	σ^+	0.68 (1F)	Addition: CCl_2 I_2	113
19. $XC_6H_4(CH{=}CH)_nCH{=}NC_6H_4Y$	pK_a	σ^+	0.76 (1F) 0.72 (1F)	Y=H Y=*n*-OCH_3	202
20. $Ar(CH{=}CH)_nArNH_2$	*k*	σ	0.63 (1F) 0.67 (1F)	Acylation	98
21. $R_1(CH{=}CH)_nCOR_2^{**}$ *S-cis-* *S-trans-*			0.766±0.012 (1F) 0.855±0.024 (1F)		10

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*The values of ρ_{rel} are quoted.

**Series 21 includes cinnamaldehydes, chalcones, styrylketones, cinnamic acids and their esters, dimethylamides, etc.

The dependence of the π'_{1F} on the nature of the property being correlated is very clearly manifested. Thus π'_{1F} for the ketones $XC_6H_4(CH{=}CH)_nCOCH_3$ amounts to 0.47 (*S-cis*-conformers) or 0.54 (*S-trans*-conformers) on the basis of the correlation analysis of ν(CO) and 0.76 on the basis of the correlation of half-wave potentials. The difference between the values of π'_{1F} is apparently determined by the different sensitivities of the properties to the influence of substituents.

The dependence of the values of π'_{1F} on the conformation of the molecules was already noted above (see, for example, series 4, 6, and 22 in Table 14): *S-trans*-conformers are appreciably more sensitive to the influence of substituents. This apparently applies also to geometrical isomers: a *trans*-double bond transmits the influence of a substituent more effectively than a *cis*-double bond (series 11).

In some cases π'_{1F} is affected by the solvent in which the property to be correlated has been determined [see the difference between the values of π'_{1F} found from the correlation analysis of the ν(CO) determined in CCl_4 and $CHCL_3$ (series 2 and 6) or between the values found from the correlation analysis of the half-wave potentials determined in water and dimethylformamide (series 12)]. This may be associated with the different degrees of solvation of the bridge or of the reaction centre or with the specific interaction of the substance with the solvent.

The values of π'_{1F}, π'_{2F}, π'_{3F}, and π'_{4F}, obtained from the correlation analysis of the same parameters [ν(CO), μ, λ_{max}, $E_{\frac{1}{2}}$, and k] of the polyene series 1, 2, 3, 10, and 11, are linked by the relation [44]

$$\pi'_{1F} : \pi'_{2F} : \pi'_{3F} : \pi'_{4F} = \pi'_{1F} : (\pi'_{1F})^2 : (\pi'_{1F})^3 : (\pi'_{1F})^4. \qquad (10)$$

Thus the influence of substituents diminishes in a geometrical progression with increase of the number of double bonds.

This conclusion agrees fully with data obtained by Bowden[71], who believed that π' is a power function of the type

$$\pi' = \varepsilon^n, \qquad (11)$$

where ϵ is the transmission factor of the atomic group entering into the composition of the bridge and n the number of such atomic groups, and calculated on the basis of the analysis of 17 reaction series the values of ϵ for the carbon atom in the sp^3 (0.48 ± 0.04), sp^2 (0.67 ± 0.02), and sp (0.57 ± 0.01) states, and found that π'_{1F} for the $-CH{=}CH-$ group is equal to ϵ^2 (C_{sp^2} = 0.45). If Eqn. (11) holds, then evidently $\pi'_{2F} = (\pi'_{1F})^2$, $\pi'_{3F} = (\pi'_{1F})^3$, and $\pi'_{4F} = (\pi'_{1F})^4$, i.e. Eqn. (10), found in the correlation analysis of the experimental properties of polyenes, is obtained. The validity of Eqn. (10) indicates the equivalence of the double bonds with respect to the transmission of the influence of substituents in these polyenes.

It is of interest that the values of ρ_{rel} (see Table 14, series 16) [107] are in the following proportions:

$0.66 : 0.30 : 0.18 = 0.66 : (0.66)^3 : (0.66)^4$.

Table 15. The calculated and experimental values of $10^3\,\nu_{max}$ (cm^{-1}) and $E_{\frac{1}{2}}$ (V) for certain series of $C_6H_5(CH{=}CH)_n$. CHO polyenes.

Property	*n*						
	0	1	2	3	4	5	6
ν_{max} (expt.)	40.7	34.5	30.9	28.0	25.6	24.6	23.0
ν_{max} (calc.)	—	34.6	30.5	25.2	23.4	21.6	20.9
$E_{1/2}$ (expt.)	1.36	1.09	0.89	0.77	0.70	0.60	
$E_{1/2}$ (calc.)	—	1.15	0.98	0.83	0.69	0.59	
			$(CH_3)_2N(CH{=}CH)_nCHO$				
ν_{max} (expt.)	—	35.4	27.7	23.7	21.8	20.4	19.2
ν_{max} (calc.)	—	—	30.3	25.4	21.6	18.6	15.8
			p-$CH_3OC_6H_4(CH{=}CH)_nCHO$				
ν_{max} (expt.)	—	31.1	28.4	26.2	24.9	23.6	22.7
ν_{max} (calc.)	—	—	26.3	24.0	22.2	21.0	20.0

However, Eqn. (10) does not hold for series 6 (see Table 14, data for the correlation of Z/Z_0), which can probably be explained by the different deviations of members of this series from coplanarity[45,147,148].

One should also note that, whereas the π-electron densities q_0 at the carbonyl oxygen atom in the aldehyde series 1 are correlated with the σ_R^0 constants and the values of π'_{1F}, π'_{2F}, and π'_{3F} found from these data obey Eqn. (10), the π-electron densities at the oxygen atom of the keto-group in chalcones and their vinylogues (series 6) are almost independent of the nature of the substituent X.[45]

Comparison of the values of π'_{1F} and π''_{1F} determined for similar series (Table 14, series 6 and 8, 9 and 13, and 11 and 14) in the correlation analysis of identical properties shows that the efficiency of the transmission of influences via a double bond is somewhat greater than via a triple bond.

Using Eqn. (10) and knowing the value of π'_{1F} for the given series, it is possible to calculate beforehand the properties of compounds with 2–5 and even 6 double bonds. Table 15 presents examples of such calculations[44]. Evidently the agreement between calculation and experiment is satisfactory.

As regards the mechanism of the transmission of influences, analysis of the data in Table 14 shows that the best correlation is achieved in most cases when the σ^+, σ_R^+, and σ_R^0 constants are used, i.e. the mesomeric mechanism is most important in the transmission of influences via multiple bonds. A detailed analysis of the two-parameter equation for aliphatic compounds with a single bond has been made by Charton[7]. Table 16 lists the contributions of the mesomeric effect (P_R) to the overall electronic effect of the substituent for a number of typical series. Evidently the contribution is large in most cases. It is striking that P can be influenced by the solvent in which the properties being correlated are determined (Table 16, series 4, 5, and 11).

Table 16. The mechanism of the transmission of influences via multiple bonds [the values of P_R (%) for certain series[7]].

Series	Property	P_R, %	Remarks
1. $XCH = CH_2$	μ	42	
	I	66–69	
	ν	78	Frequency in ^1H NMR spectrum
	δ	53	
	k	37	Addition of Cl_2 to CH_3COOH
	"	21	Addition of Br_2 to CH_3COOH
	"	52	Reaction with $C_6H_5CH = CHCHO$ in dioxan
2. $XCH = CHBr$	μ	42	
	δ	64	
3. $C_6H_5CH = CHX$		44	
4. $XCH = CHCOOH$ *trans-*	pK_a	48	In water
	"	56	In 80% methylcellosolve
	"	75	In 50% alcohol
	k	42–50	Esterification of $(C_6H_5)_2CN_2$ in alcohol
	"	51	Ditto in t-butyl alcohol or ethyl acetate
5. $XCH = CHCOOH$ *cis-*	pK_a	39	In water
	"	71	In 50% alcohol
	k	55	Esterification of $(C_6H_5)_2CN_2$ in ethyl acetate
6. $CH_3C(X) = CHCOOH$ *cis-* *trans-*	pK_a	55	In water
	"	45	Ditto
7. $C_6H_5C(X) = CHCOOH$ *cis-* *trans-*	pK_a	49	In 50% alcohol
	"	59	Ditto
8. $XCH = CHCOOCH_3$	δ	50	Addition to 9,10-dimethylanthracene in dioxan
	k	95	
9. $XCH = CHCOOC_2H_5$	k	63	Alkaline hydrolysis in water
	"	52	Ditto in 70% dioxan

The two-parameter Eqn. (4) and a similar two-parameter equation including the cross term,

$$Q = Q_0 + \alpha\sigma_I + \beta\sigma_R^+ + \gamma\sigma_I\sigma_R^+, \qquad (12)$$

have been used to estimate the contributions of the inductive and mesomeric effects for series 1, 3, and 6 (see Table 14)[44,45]. It was found that, in the

$X(CH=CH)_nCHO$ polyenal series 1, the inductive effect makes the greatest contribution ($n = 1$, $\rho_I \gg \rho_R^+$), while for the remaining series ($n = 2-4$) the mesomeric effect assumes the greatest importance, as expected, because of the rapid decay of the inductive effect. Similar data were obtained also for series 3. One should note that in all the examples application of Eqn. (12) yielded very high cross terms, which shows that the changes in the transmission of inductive and mesomeric effects are probably not quite so independent as is usually believed[20,21].

The application of the two-parameter Eqn. (12) to the series of chalcones and their vinylogues (Table 14, series 6) showed that the inductive effect predominates ($\rho_I > \rho_R^+$) in series with $n = 1-3$; this is consistent with the fact that these compounds are not planar.

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The Capacity of Lactams for Polymerisation as a Function of Their Structure

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The capacity of lactams of different structures for polymerisation is considered from thermodynamic and kinetic standpoints. It is shown that the significant differences between the enthalpies of polymerisation can be accounted for by the presence of intramolecular hydrogen bonds and also by the resonance stabilisation of the cyclic amide. The probability of the polymerisation of lactams is determined kinetically by the chemical structure of the monomer, namely the conformation of the molecules (the presence of *cis-* and *trans-*isomers), the stabilisation of the amide group by the inductive, mesomeric, and hyperconjugation effects, the polarity of the molecules (the presence of hydrogen bonds or the occurrence of dipole-dipole interactions), and the basicity of the monomer.

The bibliography includes 126 references.

CONTENTS

I. INTRODUCTION

Synthetic heterochain polyamides constitute a class of macromolecular compounds comprising an enormous number of examples and having considerable theoretical and practical importance[1]. Together with the polycondensation reaction, the polymerisation of lactams (cyclic amides) is very important for the synthesis of polyamides. During the last decade, considerable advances have been made in the field of the polymerisation and synthesis of lactams: new methods for their polymerisation have been developed and the range of lactams used to synthesise industrial polyamides (β-lactams, α-pyrrolidinone, α-piperidinone, and ω-dodecalactam) has been extended.

The anionic polymerisation of lactams, on the basis of which a procedure has been developed for the synthesis of polyamide articles by chemical moulding[2,3], which is a great achievement in the synthesis and processing of polymers, has developed particularly in recent years. The use of the ionic polymerisation of lactams made it possible to extend the scope of the synthesis of polyamides having different structures. The method has been used to synthesise both homopolyamides (with linear, branched, and cross-linked structures[4-8]) and copolymers (statistical[9-12], block[13,14], and graft[15-19]), the properties of which vary within wide limits as a function of their structure and the initial monomers.

In connection with the expansion of the range of lactams used to synthesise various types of polyamides, the problem of the dependence of their reactivity on structure has become important. Extensive experimental data have accumulated in the literature on the reactivity of lactams, treated from both thermodynamic and kinetic standpoints, and a number of reviews have been published on the mechanism and kinetics of polymerisation in the presence of various catalytic systems[20-23]. However, the problem of the extent to which the differences between the reactivities of lactams are a consequence of thermodynamic factors and to what extent they are determined by the kinetic conditions arising during these reactions still cannot be regarded as solved.

Examination of the general characteristics of the polymerisation of cyclic amides containing different numbers of units in the ring from thermodynamic and kinetic standpoints is the subject of the present review.

II. THERMODYNAMIC APPROACH

The thermodynamics of polymerisation is known to be determined solely by the propagation stage, since the initiation and chain-termination stage are single steps, while the chain propagation stage involves a large number of addition reactions. The sharp differences in the behaviour of different lactams can probably be accounted for primarily by the sign and magnitude of the free energies of polymerisation:

$$\Delta G = \Delta H - T\Delta S = \Delta G^0 + RT\ln K,$$

where ΔH is the change in the heat content of the system or the heat of reaction, ΔS the change in the entropy of the system, T the absolute temperature, K the equilibrium constant of the reaction, and ΔG° the standard change in free energy on polymerisation referred to the pure monomer and the polymer. If $\Delta G < 0$ for polymerisation, i.e. the free energy of the system decreases, the process is thermodynamically feasible.

The enthalpy of polymerisation of cyclic compounds is associated with the strain of their rings, which depends on the distortion of the valence angles and the interaction of atoms within the ring; the enthalpy depends both on ring size and the presence of substituents. For cyclic amides, ΔH can depend also on (1) the different resonance stabilisations of the monomer and polymer owing to the unequal conjugation or hyperconjugation and (2) the differences between the energies of hydrogen bonds or dipole–dipole interactions in the monomer and polymer.

The entropy of polymerisation depends on the probability of the existence of the monomer in the cyclic form or in the form of the elementary unit of the linear polymer.

1. ΔH for the Polymerisation of Lactams

The first attempt at a thermodynamic treatment of the reversible ring $\rightleftharpoons$ polymer reaction was made in 1950 by Strepikheev[24], who outlined a correct and rigorous procedure for the thermodynamic treatment of the problem of the polymerisation of cyclic compounds. A similar treatment of the thermodynamic stability of cyclic compounds was achieved independently in 1955 by Dainton et al.[25] in connection with the estimation of the free energy of the system. The values of ΔH for the hypothetical polymerisation reaction of cycloalkanes were found as the differences between the heats of formation of the polymer units (these heats were calculated from the contributions of the corresponding groups to the heat of formation) and the experimental heats of formation of cycloalkanes.

The heat of polymerisation can be found in different ways.

1. By direct calorimetric measurements on the polymerisation reaction, which make it possible to determine ΔH. However, the polymerisation process hinders calorimetric measurements, which naturally affects the accuracy of the determination.
2. By calculating ΔH from a comparison of the heats of combustion of the monomer and polymer. The latter quantity is calculated per polymer unit. The accuracy of this method is also low, since a small value of ΔH is calculated from [the difference between] large quantities.
3. By determining the difference between the experimental heats of combustion of the lactams and the heats of combustion calculated additively from the increments for the corresponding groups: 155.85 kcal mole^{-1} for CH_2(liq.), 79.4 kcal mole^{-1} for CONH(liq.), 156.3 kcal mole^{-1} for CH_2(solid), and 77.2 kcal mole^{-1} for CONH(solid).

Table 1. Heats of combustion and ring strain in cycloalkanes[26].

No. of ring units n	Heat of combustion per methylene group, kcal mole^{-1}	Ring strain* per methylene group, kcal mole^{-1}	No. of ring units n	Heat of combustion per methylene group, kcal mole^{-1}	Ring strain* per methylene group, kcal mole^{-1}
3	166.6	9.2	9	158.8	1.4
4	164.0	6.6	10	158.6	1.2
5	158.7	1.3	11	158.4	1.0
6	157.4	0.0	12	157.7	0.3
7	158.3	0.9	13	157.8	0.4
8	158.6	1.2	n-alkane	157.4	0.0

* Ring strain is defined as the difference between the heats of combustion per methylene group of the given cycloalkane and the [corresponding?] n-alkane (157.4 kcal mole^{-1}).

We shall consider initially the thermodynamic stability of cycloalkanes. Comparison of the heats of combustion per methylene group in such cyclic compounds and linear alkanes yields a general estimate of a thermodynamic stability of rings of different size.[26] Table 1 shows that the differences between the heats of combustion of cycloalkanes and n-alkanes per methylene group demonstrate a decrease of thermodynamic stability with increase in ring strain. The strain in three- and four-membered rings is very high, diminishing subsequently on passing to five-, six-, and seven-membered rings, after which it again increases for eight to eleven-membered rings, and finally falls once more on passing to rings of still greater size.

Two components of ring strain are distinguished: angular strain and repulsion due to the presence of substituents. Rings containing less than five atoms are highly strained through high angular strain, i.e. the considerable distortion of their valence angles compared with the normal tetrahedral angle. In five-membered and larger rings, there is no distortion of the valence angle, since the rings can exist in a non-planar form. In rings with more than eight units, the strain due to the distortion of the valence angle is virtually absent, but they are nevertheless thermodynamically unstable, because the hydrogen atoms or other substituents are contained within the ring at distances such that they repel one another. On this basis, it is possible to set up the following sequence of cycloalkanes as a function of ring size in order of increasing thermodynamic stability:

$$3{,}4 < 8-11 < 7{,}12{,}13 < 5 < 6.$$

Rings containing certain other atoms or groups of atoms instead of methylene groups fall in the same sequence. Although the data for cyclic compounds such as ethers, lactones, and lactams are inadequate, the general postulates have been confirmed[27]. Thus Small[28] attempted to extend Dainton's calculations[25] for cycloalkanes to certain series of saturated heterocyclic compounds (cyclic ethers and imines). He showed that the difference between the values of ΔS for the polymerisation reactions of cycloalkanes and the corresponding cyclic ethers and imines is small. The ΔH for the polymerisation reaction show greater differences.

Hall and Schneider[29] confirmed the validity of Dainton's[25] and Small's[28] findings and reached the following conclusions concerning the capacity of various heterocyclic compounds for polymerisation on the basis of their own experimental data.

1. Four-, seven-, and eight-membered cyclic compounds polymerise most readily; the capacity of five- and six-membered carbonyl monomers for polymerisation depends on the class of compound.
2. Substitution of cyclic hydrocarbons by a heteroatom has an insignificant influence on their capacity for polymerisation.
3. Substituents (alkyl or aryl) always decrease the capacity of cyclic compounds for polymerisation.

Other workers[30] also established that the substitution of a CH_2 group by O or NH causes little alteration in the capacity of cyclic compounds for polymerisation. In this case, substitution has hardly any influence on the valence angles in cyclic structures. The ring strain caused by the repulsion of substituents diminishes when the methylene group is replaced by the less bulky carbonyl group or an oxygen atom, which leads to an increase of the thermodynamic stability of the ring. It has also been shown[27] that, in contrast to hydrogen, other substituents in cyclic structures as a rule increase their stability, although the cause of this is not altogether clear.

We shall now consider the variation of the heats of polymerisation of lactams with different numbers of units in the ring. Skuratov and Strepikheev and coworkers[31-38, 43-45] have played a leading role in the study of this problem. Table 2 presents the values of ΔH for the polymerisation of lactams containing between 5 and 13 units in the ring and obtained in different ways. Column *A* lists the ΔH for the polymerisation of lactams measured experimentally with the aid of a double calorimeter using a compensation technique; column *B* lists the ΔH estimated by another procedure—by comparing the experimental heats of combustion of lactams and the corresponding polymers: the ΔH calculated from the enthalpies of cyclisation of different lactams are given in column *C*.

Table 2. Heats of polymerisation of lactams.

Lactam	No. of ring units *n*	ΔH, kcal mole^{-1}	Refs.	ΔH, kcal mole^{-1}	Refs.	ΔH, kcal mole^{-1}	Refs.
		A		*B*		*C*	
α-Pyrrolidinone	5	—	—	+1.3	32,33	−1.1	33
				−1.3	41,42		
α-Piperidinone	6	—	—	−1.1	32,33	−2.2	33
ε-Caprolactam	7	−3.3	34	−3.0	32,33	−3.8	33
		−3.5	39		38,39		
ζ-Oenantholactam	8	−5.2	35	−5.7	32,33,38,42	−5.3	33
η-Caprylolactam	9	−7.8	33	−9.6	38,42	—	—
Pelargolactam	10	—	—	—	—	−5.5	38
Decanolactam	11	—	—	—	—	−2.8	38
Undecanolactam	12	—	—	—	—	+0.5	38
Laurolactam	13	~0	33,38	−1.5	41,42	—	—

It was to be expected that the ΔH for the polymerisation of lactams estimated in different ways should be different, depending on the temperature and the phase state of the monomers and polymers to which they refer. However, Table 2 shows that the values of ΔH are similar. Therefore, in order to calculate ΔH for polymerisation, it is quite admissible to adopt the average of these values (Fig. 1). The ΔH for the polymerisation of lactams have been calculated in this way[38]. Fig. 1 shows that ΔH for the polymerisation of lactams containing between 5 and 9 units in the ring decreases and then rises for lactams containing between 9 and 13 units in the ring to values close to zero.

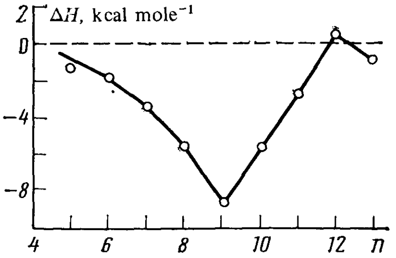
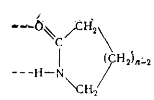


Figure 1. The heats of polymerisation of lactams (ΔH) as a function of the number of units in the ring (n).

Comparison of the heats of polymerisation of lactams and the corresponding cycloalkanes shows that the enthalpies of lactam ring formation are smaller than the values for their hydrocarbon analogues (Table 3).

Some workers believe[46-50] that such a significant difference between the enthalpies of polymerisation of lactams and cycloalkanes can be accounted for by the presence of intermolecular hydrogen bonds in the lactams†. A comparative study of the free and associated NH groups by infrared spectroscopy led to conclusions about the isomerism and conformations of the rings of the test compounds:


cis-conformation

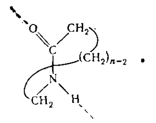

trans-conformation

Table 3. Comparison of the enthalpies of polymerisation of cycloalkanes and cyclic amides.

No. of ring units *n*	ΔH, kcal mole^{-1}	
	cycloalkane (Ref.25)	lactam (Ref.33)
5	5.2	1.1
7	5.2	3.8
8	8.3	5.3

The energy of formation of intermolecular hydrogen bonds is expressed in terms of quantities of the same order of magnitude as the heat of ring opening and can vary within wide limits depending on the structure of the lactam (Table 4). Table 4 shows that α-pyrrolidinone exists exclusively in the form of the *cis*-isomers. Lactams containing between 6 and 9 units in the ring exist in both *cis*- and *trans*-forms, while (10–13)-membered lactams exist in the thermodynamically more stable (ΔH_{av} = −4.0 kcal mole^{-1}) isomeric *trans*-form.

Table 4. Thermodynamic characteristics of the hydrogen bonds in lactams[47].

No. of ring units *n*	$-\Delta H$, kcal mole^{-1}	
	cis-	*trans-*
5	8.35	—
6	7.30	3.90
7	7.10	4.20
8	6.95	3.70
9	7.05	5.05
10	—	3.82
11	—	3.82
12	—	3.80
13	—	3.75
	mean 7.35	mean . 4.00

According to Ogata's data[50], the *cis*-form is characteristic of (6–7)-membered lactams, ζ-oenantholactam contains equivalent amounts of the *cis*- and *trans*-isomers, and the nine-membered lactam exists preferentially in the *trans*-form. On the basis of Ogata's data, one can calculate, subject to a major assumption and without allowance

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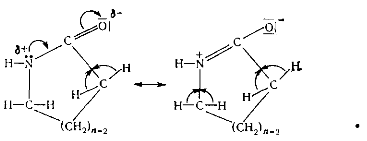
† The intermolecular interaction in the polymer does not play an appreciable role owing to steric factors[27].

for resonance stabilisation, the maximum degree of association of lactam molecules. If it assumed arbitrarily that ΔH for cyclo-octane is approximately equal to ΔH_{tot} for ζ-oenantholactam, then the degree of association of the molecules x can be found as follows:

$$\Delta H_{\text{cyclo-octane}} \simeq \Delta H_{\zeta\text{-oenantholactam}} + \frac{x}{2}(\Delta H_{\text{cis-}} + \Delta H_{\text{trans}});$$

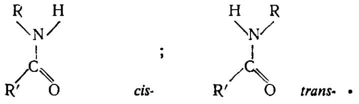
$x = 56.3\%$. We believe that this value is very much too high.

Thus the reduced enthalpy of polymerisation of lactam rings compared with the hydrocarbon analogues cannot be fully accounted for by the energy of formation of intermolecular hydrogen bonds in lactam molecules. Evidently the lower isothermal heat of polymerisation (negative ΔH) of lactams compared with the corresponding [hydrocarbon] ring is also associated with the resonance stabilisation of the lactam, since resonance is possible only in the monomer[27]:

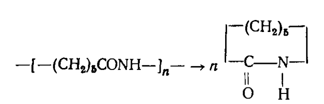


Other workers hold the same view[48-51]. Furthermore, owing to the hyperconjugation of the methylene group with the C=O and C=N bonds, ΔH for the polymerisation of lactams is reduced.

A novel method for the empirical calculation of ΔH for lactams from the change in the number of the so called "*gauche*-interactions" of the butane type on ring closure is discussed by Cubbon[52] in connection with the estimation of the influence of substituents on the polymerisation of lactams. He also believes that, when a seven-membered lactam cyclises, four new *gauche*-interactions occur (two involving CH_2/CH_2 groups, one involving the CH_2/CO group, and one involving the CH_2/NH group). The energy of a single interaction is 0.8 kcal mole^{-1}, so that the total contribution to the enthalpy of cyclisation of ε-caprolactam is 3.2 kcal mole^{-1}. A ^{1}H NMR study of methylacetamide has shown that the *trans*-form of the amide group is more stable than the *cis*-form at least to the extent of 1.4 kcal mole^{-1}:[52]



On the other hand, the overall enthalpy of the reaction



$$-[-(CH_2)_5CONH-]_n- \rightarrow n\ \overbrace{\underset{\overset{\|}{O}}{C}-\underset{|}{\overset{}{N}}H}^{(CH_2)_5}$$

is approximately 4.6 kcal mole^{-1}. We believe that this value is not altogether correct, since it is difficult to accept that ε-caprolactam exists exclusively in the *cis*-form (see above).

2. Estimation of ΔS for the Polymerisation of Lactams (under Standard Conditions)

One of the methods for the calculation of ΔS is based on the determination of the equilibrium constant within the limits of a certain temperature range. However, this method cannot be always applied, because it is difficult to measure the quantity

$$K = \frac{[M_{n+1}^-]}{[M_n^-][M]}.$$

Owing to the presence of a range of molecular weights, the number of terms (n) varies within wide limits.

The method for the determination of the entropy of polymerisation by means of the formula

$$\Delta S^0 = \Delta H^0 / T_{\text{lim}}$$

is promising. The scope of this method is limited only by the accuracy of the measurement of the heat of polymerisation and of the limiting temperature (T_{lim}).

Another, perhaps the most widely used method of calculation is based on the knowledge of the entropies of the monomer and polymer:

$$\Delta S^0 = \frac{1}{n} \cdot S^0_{(n)} - S^0_{(1)},$$

where $S^0_{(n)}$(polymers) and $S^0_{(1)}$(monomers) are calculated from the experimental true heat capacities of these substances at low temperatures.

There exists a method for the calculation of ΔS° using the relation

$$\Delta S^0 = R \ln \frac{k_p}{k_{p^1}},$$

which follows directly from the expressions for the propagation (k_p) and depolymerisation (k_{p^1}) rate constants.

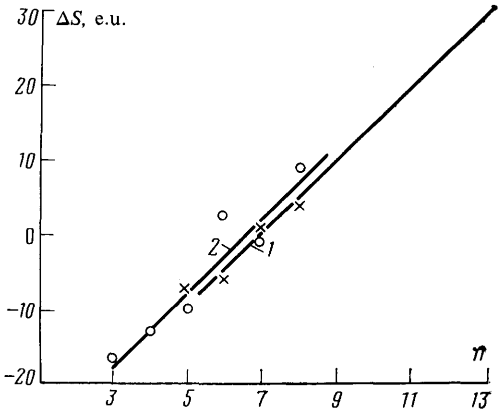


Figure 2. Variation of ΔS for the polymerisation of lactams and cycloalkanes as a function of the number of units in the ring under standard conditions: 1) lactams[38]; 2) cycloalkanes[25].

ΔS can also be obtained by a statistical procedure. In this case one uses the relation according to which the overall entropy of reaction consists of ΔS_{trans}, ΔS_{rot}, and ΔS_{vibr}.

There are very few literature data for the entropies of lactams with different numbers of units in the ring and the corresponding polymers, while for (9–13)-membered lactams there are no data at all.

Skuratov[32,38,44,45], who carried out the most systematic studies on this problem, estimated the entropies of polymerisation of five-, six-, seven-, and eight-membered cyclic amides. The ΔS were calculated from the absolute entropies $S_{298\cdot16}$ and the true heat capacities of these substances in the temperature range 62–328 K. The values of ΔS for (9–13)-membered lactams were found[38] by the linear extrapolation of the values for (5–8)-membered lactams (Fig. 2) in view of the fact that the ΔS obtained for the polymerisation of (5–8)-membered lactams fit satisfactorily on a straight line. These results are naturally extremely approximate.

It is noteworthy that the ΔS for the hypothetical polymerisation of cycloalkanes containing between 3 and 8 units in the ring (except cyclohexane) also vary linearly with the number of such units (Fig. 2, curve *2*).

3. Estimation of ΔG for the Polymerisation of Lactams (under Standard Conditions)

The free energies of polymerisation ΔG of lactams containing between 5 and 13 ring units are presented in Table 5. Evidently ΔG for the polymerisation reaction varies from a positive value (for the five-membered ring) and a value close to zero (for a six-membered lactam) to negative values, which reach a maximum for (9–10)-membered lactams, and then falls somewhat. The polymerisation of α-pyrrolidinone and α-piperidinone is exothermic (negative ΔH) and exoentropic (negative ΔS). The negative ΔS for the polymerisation of five- and six-membered lactams is probably due to the fact that the number of degrees of freedom diminishes on passing from the monomer to the polymer. Consequently the polymerisation of five- and six-membered lactams is favourable from the standpoint of the enthalpy factor but not on entropy grounds. For seven- and eight-membered lactams, the main contribution to ΔG for the polymerisation reaction comes from the enthalpy term, for nine-, ten-, and eleven-membered lactams the contributions of ΔH and ΔS are approximately the same, while for twelve- and thirteen-membered cyclic amides ΔH for the polymerisation reaction is negligible and the polymerisation proceeds mainly as a result of the entropy change.

Table 5. Free energies of polymerisation ΔG of lactams with different numbers of ring units.

No. of ring units n	ΔH *, kcal mole^{-1}	ΔS^{38}	$T\cdot\Delta S_{298,16}$, kcal mole^{-1}	ΔG, kcal mole^{-1}
5	−1.1	−7.3	−2.2	1.1
6	−1.7	−6.0	−1.8	0.1
7	−3.3	1.1	0.3	−3.6
8	−5.4	4.0	1.2	−6.6
9	−8.4	10.0	3.0	−11.4
10	−5.6	15.0	4.5	−10.1
11	−2.8	20.0	6.0	−8.8
12	0.5	25.0	7.5	−7.0
13	−0.7	30.0	9.0	−9.7

*The average values of ΔH obtained from the results of different workers are quoted (see Table 2).

Fig. 3 presents the values of ΔG for the polymerisation of lactams and cycloalkanes[25] as a function of the number of ring units. It is seen that the variation of ΔG for the polymerisation of lactams and cycloalkanes is very similar. The values of ΔG for five- and six-membered rings are close to zero, becoming negative for larger rings. Using the equation

$$\ln[\mathrm{M}]_c = \frac{\Delta H^0}{R\,T_{\lim}} - \frac{\Delta S^0}{R},$$

expressing the dependence of the equilibrium (critical) concentration of the monomer $[\mathrm{M}]_c$ on the limiting polymerisation temperature[27], we calculated the critical monomer concentrations at 25°C (Table 6); the limiting temperatures for six- and seven-membered lactams are also quoted.

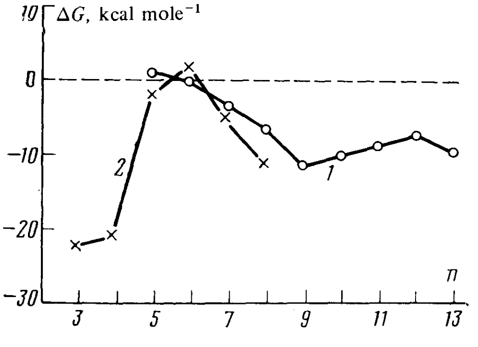


Figure 3. Variation of ΔG for the polymerisation of lactams (curve *1*) and cycloalkanes (curve *2*) as a function of the number of units in the ring (*n*).

Table 6. The "polymerisation ⇌ depolymerisation" equilibrium.

Lactam	$[\mathrm{M}]_c$ at 25°C, M	$T_{\lim}$ for pure monomer, °C
α-Pyrrolidinone	6,3	—
α-Piperidinone	1,2	60[53]
ε-Caprolactam	$2.1\cdot10^{-3}$	254[54]
ξ-Oenantholactam	$1.4\cdot10^{-5}$	—
η-Caprylolactam	$4.3\cdot10^{-9}$	—
Pelargolactam	$4.0\cdot10^{-8}$	—
Decanolactam	$3.6\cdot10^{-7}$	—
Undecanolactam	$7.8\cdot10^{-6}$	—
Laurolactam	$8.2\cdot10^{-8}$	

Since ΔH° is negative, the concentration of the monomer in equilibrium with the polymer increases with temperature and the relation between $\ln[\mathrm{M}]_c$ and $1/T$ is represented by a straight line with a negative slope (slope = $\Delta H^\circ/R$) making an intercept on the ordinate axis equal to $\Delta S^\circ/R$ (Fig. 4). The data presented in Table 6 and in Fig. 4 indicate high critical concentrations in the "polymerisation ⇌ depolymerisation" equilibrium for five- and six-membered lactams, which ultimately determines the comparatively low equilibrium degree of polymerisation of the lactams.

Thus one may conclude that the polymerisation of (7–13)-membered lactams is thermodynamically feasible (ΔG is negative). The small positive values of ΔG for the polymerisation of α-pyrrolidinone and α-piperidinone and the extremely large errors of the determination of the thermodynamic characteristics preclude a conclusion concerning the thermodynamic feasibility of the polymerisation of five- and six-membered cyclic amides.

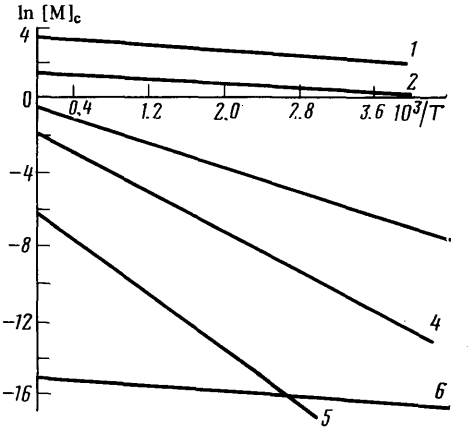


Figure 4. Variation of ln [M]c with $1/T$ in the polymerisation of lactams with different numbers of units in the ring: 1) α-pyrrolidinone; 2) α-piperidinone; 3) ϵ-caprolactam; 4) ζ-oenantholactam; 5) η-caprylolactam; 6) laurolactam.

Taking into account the thermodynamic factors only, it is possible to set up a series based on the reactivities of the lactams as a function of ring size:

$$9>10>13>11>12>8>7\gg 6,5.$$

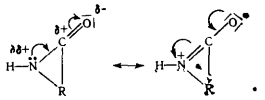
III. KINETIC APPROACH

The negative value of ΔG does not, however, imply that polymerisation is possible under any conditions. The probability of achieving thermodynamically allowed polymerisation depends on its being allowed by kinetic factors, i.e. on whether or not the given process occurs at an appreciable rate under the chosen reaction conditions. The kinetic capacity of monomers for polymerisation is determined by the mobility of the corresponding bonds under the reaction conditions, since thermodynamically unstable compounds can be kinetically quite stable and may not polymerise if they do not contain a labile bond.

One may quote as an example cycloalkanes for which it has been as yet impossible to find polymerisation conditions despite their considerable thermodynamic instability[25,55].

1. The Chemical Structure of the Monomer

Heterocyclic compounds to which lactams belong are capable of selective ring opening at the site of the heterobond. However, this fact is not related to the lower energetic stability of the heterobond compared with the C−C bond (the energy of the C−C bond is 63 kcal mole^{-1}, that of the C−N bond 66 kcal mole^{-1}, and that of the C−O bond 79 kcal mole^{-1}), but is associated with its susceptibility to polarisation under the influence of various chemical agents. The polarisability of the lactam ring can be represented schematically as follows:



The electron-accepting carbonyl group causes a shift of electron density (the $-M$ effect; the inductive effect of the N−H bond may be neglected), as a result of which the amide group is polarised. The possibility of the hyperconjugation effect in the lactam molecule was discussed above.

The presence of the resonance effect in the amide group has been demonstrated by Pauling and Corey[56], who carried out a very thorough investigation of the NH−CO group by X-ray diffraction. The bond angles and interatomic distances in amides are presented in Fig. 5.

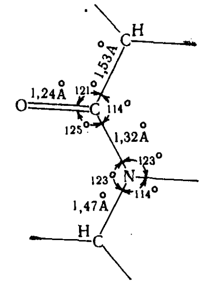
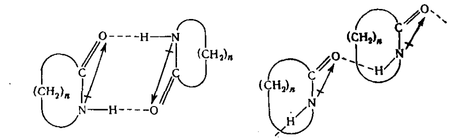


Figure 5. Amide linkages[56].

It is evident from Fig. 5 that the C−N bond length in the amide group is shorter than the normal length of the isolated C−N bond, which is 1.5 Å. This result demonstrates a certain amount of double bond character of this linkage. In this case the NH−CO group is planar and all its valence bonds, illustrated in Fig. 5, lie in the plane of the figure; this in fact permits the existence of the *cis*- and *trans*-forms (see above).

The existence of the *cis*- and *trans*-configurations of lactams can be observed by measuring the dielectric constants of their benzene solutions at variable concentrations. Like the acyclic amides, the *cis*-lactam forms a hydrogen-bonded dimer, in which the two electric moments (arrows in the formula) mutually cancel out.


cis-lactam *trans*-lactam

With increase of concentration, the degree of association of the molecules rises and, in the case of the *cis*-lactam, the dielectric constant falls. On the other hand, the *trans*-lactam can form only a linear associated species in which the electric moments are additively combined and the dielectric constant of the benzene solution therefore increases with concentration.

The dipole moments of lactams presented in Table 7 show that they depend little on the number of units in the lactam ring, although the dipole moment of the five-membered lactam is somewhat reduced.

Table 7. The dipole moments of lactams[57] (measured in benzene).

No. of ring units n	5	6	7	8	9	10	11	13
Dipole moment, D	3.55	3.83	3.88	3.86	3.85	3.79	3.78	3.78

Here it is appropriate to examine the studies by Ogata[48-50], devoted to the influence of the resonance effect of the amide group on the ability of lactams to polymerise. He investigated the addition of hydrogen chloride to certain cyclic and linear amides by infrared spectroscopy. The constant for the equilibrium between the amide group and HCl was calculated from the equation

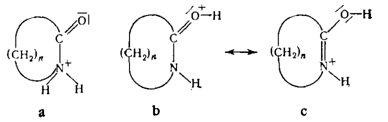
$$K = \frac{[-\overset{+}{N}H_2CO-]}{[-NHCO-]\cdot[H^+]} .$$

Table 8. The equilibrium constants and heats of addition of hydrogen chloride to the amide group[50].

Amide derivative	K			$-\Delta H$, kcal mole^{-1}
	20° C	40° C	55° C	
α-Pyrrolidinone	159	68	—	7.64
α-Piperidinone	164	79	—	6.58
ε-Caprolactam	177	124	91	3.15
ξ-Oenantholactam	107	82	82	1.63
Decanolactam	83	45	45	3.70
N-Methyl-α-piperidinone	49	38	—	2.34
N-Methyl-ε-caprolactam	35	20	12	5.12
NN'-Dibutylacetamide	35	22	—	4.14
N-Hexylacetamide	58	48	—	2.16

The heats of addition of HCl to the amide were calculated from the slope of the curve describing the linear relation between ln$K$ and the equilibrium values of the absolute temperature. Table 8 lists the average equilibrium constants for the above addition reaction involving several amide compounds. On the basis of the results, the author reaches a conclusion concerning the relative basicities of lactams. He believes[50] that seven- and eight-membered lactams are the most basic. With increase in the size of the lactam ring, its basicity falls, as can be seen from Table 8. The capacity of the five- and six-membered rings for protonation is also lower than that of the seven-membered lactam. In view of the disappearance of the characteristic $>$N–H absorption frequency and the appearance of a new frequency characteristic of the $>$NH$_2$ absorption, Ogata concludes that the proton adds to the nitrogen atom of the amide group.

We may note that the protonation of nitrogen (structure a) leads to the disappearance of resonance stabilisation, while the protonation of oxygen does not (structures b and c):



The system with protonated oxygen should therefore be more stable. Nevertheless many investigators[58,59] share Ogata's view concerning the protonation of nitrogen in the amide group of the lactam.

It was stated above that, according to Ogata[49,50], the eight-membered lactam contains equivalent amounts of the *cis*- and *trans*-forms. On this basis, the author concludes that, if the amounts of the two conformations of the amide group become equal, the resonance effect in this group diminishes with a consequent increase of the capacity of the lactams for polymerisation, which we believe to be unlikely. It was shown above that the resonance effect in the amide group of the lactam plays a certain role in the estimation of the reactivity of cyclic amides, but it is by no means decisive.

Thus the kinetic probability of the polymerisation of lactams is to a large extent determined by the chemical structure of the monomer, namely:

(1) by the conformation of the molecules (the presence of *cis*- and *trans*-isomers);

(2) by the stabilisation of the amide group due to the mesomeric, inductive and hyperconjugation effects;

(3) by the polarity of the molecules (the presence of hydrogen bonds or the occurrence of dipole–dipole interactions);

(4) by the basicity of the monomer.

2. The Capacity of Lactams for Polymerisation as a Function of the Type of Initiation

The type of initiator—a radical, cation, or anion—most suitable in a particular instance depends on the chemical structure of the monomer.

There is no information in the literature about the radical polymerisation of lactams. It has proved possible to polymerise via the cationic mechanism virtually all unsubstituted lactams with the exception of the six-membered compound. The method of ionic high-speed polymerisation of lactams made it possible to extend the range of monomers suitable for the synthesis of polyamides. Thus, α-piperidinone and α-pyrrolidinone, which were previously believed to be incapable of polymerisation[28,60,61], were in fact polymerised in the presence of anionic catalysts[62]. Ney and coworkers[63-65] achieved the anionic polymerisation of these lactams in the presence of *N*-acyl compounds and the sodium salts of the lactams on heating the reaction mixture to a temperature exceeding somewhat the melting point of the monomer, but not higher than 60°C. The introduction of an *N*-acyl compound (activator) in the polymerisation reaction made it possible to increase sharply the yield of the polymer compared with the same conditions but in the absence of the activator. Somewhat later, the polymerisation of α-pyrrolidinone were achieved by Ney in the presence of quaternary ammonium bases[66].

Barnes et al.[63] demonstrated the possibility of the polymerisation of a six-membered lactam (α-piperidinone) using the same reaction conditions as in the polymerisation of α-pyrrolidinone[65]. However, the polymerisation of α-piperidinone proceeds with much greater difficulty than that of the five-membered lactam. The above studies by Ney and coworkers are of great theoretical importance, since they established that five- and six-membered lactams, previously believed to be stable and incapable of polymerisation, are quite reactive monomers, forming polyamides under relatively mild conditions. Somewhat later, a number of other patent reports were published on the anionic polymerisation of α-pyrrolidinone[67–78] and α-piperidinone[74–78], confirming the ability of these compounds to form high-molecular-weight products.

The method of the anionic polymerisation of five- and six-lactams in the presence of activating *N*-acylamide compounds has been used successfully to polymerise various lactams containing more than six units in the ring: ϵ-caprolactam, ζ-oenantholactam, η-caprylolactam, and others. The dependence of the capacity of the monomers of polymerisation on the type of initiator is illustrated by the data in Table 9, from which it is clear that, in the presence of such initiators, polymers with a high molecular weight are formed. Although the polymerisation of five- and six-membered lactams is thermodynamically allowed, under these conditions the polymerisation of α-piperidinone is kinetically feasible only in the presence of initiators of a specific type.

Table 9. Examples of the polymerisation of lactams as a function of the type of initiation.

No. of ring units *n*	Monomer	Type of initiation			
		cationic	references	anionic	references
5	α-Pyrrolidinone	+	50	+	85—93
6	α-Piperidinone	—	50	+	85—94
7	ϵ-Caprolactam	+	50,79—81	+	85—100
8	ξ-Oenantholactam	+	81,82	+	87—102
9	η-Caprylolactam	+	79,81	+	87—102
10	Pelargolactam		—	+	87—102
11	Decanolactam	+	50	+	87—102
12	Undecanolactam		—	+	87—89,91—102
13	Laurolactam	+	83—84	+	87,88,91—102

Table 10. The capacity of lactams for polymerisation as a function of ring size.

Type of initiation	Activity series for rings of different size	References
Acetylating agent	$8.7>13\gg5.6$	53,103
Water	$8>7>11\gg5.6$	50
HCl	$7>8\simeq9\gg5.6$	85

When the capacities of lactams for polymerisation were compared as a function of ring size, it was shown that eight- and nine-membered lactams exhibit the greatest tendency towards polymerisation, that of seven-membered lactams being somewhat inferior; the capacity of five- and six-membered lactams for polymerisation is much smaller, particularly that of the six-membered lactams (the available data are presented in Table 10).

The lactam reactivity series is close to the series expected on the basis of the measured free energies, although there are differences. Thus, according to Ogata's data[50], the thermodynamically less stable eleven-membered lactam is less reactive in cationic polymerisation than the thermodynamically more stable seven-membered lactam. We believe that the reason for this apparent anomaly may be that at 257°C ϵ-caprolactam is more reactive than the lactam of capric acid and because of the failure to attain thermodynamic equilibrium for the eleven-membered lactam under the chosen conditions, so that Ogata's data[50] correspond to the polymerisation kinetics under the chosen process conditions only. With increase of reaction temperature, the relative rates of polymerisation of the lactams would probably become equalised and it should be possible to select polymerisation conditions such that the thermodynamically less stable lactam becomes more reactive than the thermodynamically more stable lactam also from the kinetic standpoint.

It is interesting to note that five- and six-membered lactams are much more reactive under the conditions of anionic polymerisation than under the conditions of the polymerisation initiated by hydrochloric acid or water. This can be explained from the standpoint of the different mechanisms under these conditions (Fig. 6). In anionic polymerisation, the lactam ring is activated by the nucleophile. In polymerisation under the influence of water or acids, there is electrophilic attack on the lactam ring. Owing to the low electron density in the amide group, this reaction does not proceed as readily as in the presence of a nucleophile. As a result, anionic polymerisation is faster and less selective than the other two reactions.

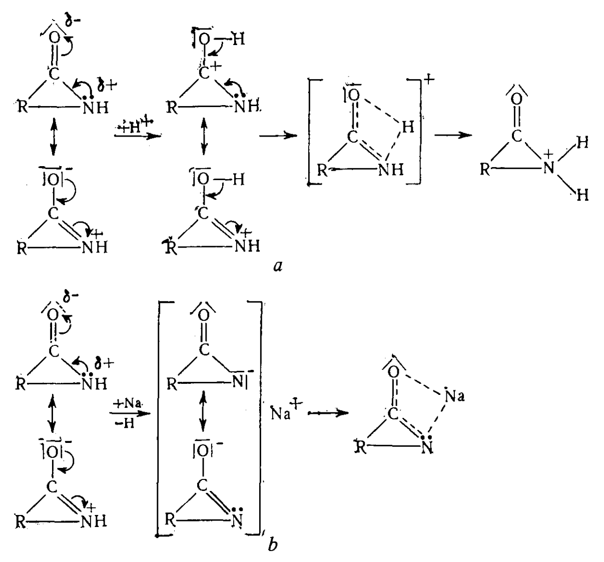


Figure 6. The mechanism of the initiation of the cationic (*a*) and anionic (*b*) polymerisation of lactams.

Lactams incapable of polymerisation in the presence of water or acids, are readily polymerised via the anionic mechanism. These differences in reactivities are also manifested when the temperatures required for polymerisation are compared. Thus polymerisation initiated by water or acid usually requires temperatures of the order of 250°C, as in other instances of cationic polymerisation. Anionic polymerisation takes place at much lower temperatures.

IV. THE INFLUENCE OF SUBSTITUENTS ON THE REACTIVITY OF LACTAMS

There are many data concerning the influence of substituents on the reactivity of lactams, which has proved to be lower than that of unsubstituted cyclic amides[104-111]. Dainton and coworkers[25,28] demonstrated by semi-empirical calculations of the free energies of the hypothetical polymerisation reactions of cycloalkanes that substitution always decreases the reactivity (Fig. 7).

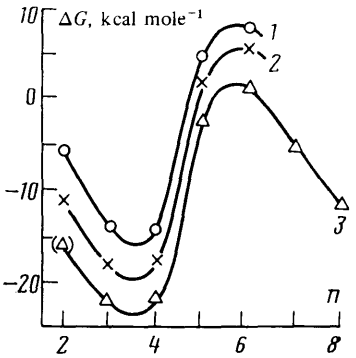


Figure 7. Variation of the free energy of polymerisation of cycloalkanes under standard conditions with ring size (n): 1) 1,1-dimethyl derivatives of cycloalkanes; 2) methyl derivatives of cycloalkanes; 3) unsubstituted cycloalkanes.

The calculations showed that the substituent in the cycloalkane ring influences the enthalpy and entropy of polymerisation of the compound with the given ring size[25,28]. The authors assumed that the results of the calculations will be valid, at least qualitatively, for the polymerisation of heterocyclic compounds, which was subsequently confirmed on the basis of extensive experimental data (Table 11).

It is seen from the Table that the influence of substituents on the capacity of lactams for polymerisation is extremely varied and depends both on the size of the substituent, its position in the ring, and the number of substituents, on the one hand, and on the size of the lactam ring, on the other.

1. *C*-Substituted Lactams

Five- and six-membered rings. Substituents are known[119] to facilitate ring closure, thereby displacing the monomer ⇌ polymer reaction equilibrium towards the monomer. Five- and six-membered lactams lose their capacity for polymerisation even in the presence of only one alkyl substituent at the carbon atom (Table 11).

The study of the cyclisation of 4-bromobutylamines has shown that substituents can greatly increase the rate of formation of the five-membered ring[120]. The estimation of the influence of the thermodynamic characteristics on the capacity of substituted lactams for polymerisation is at present difficult, since the entropies of polymerisation of these lactams are not available. According to Cubbon[52], a substituent in the lactam ring causes only a slight alteration of the entropy compared with the unsubstituted lactam, but greatly increases the entropy of cyclisation of the lactam and to a greater extent the more bulky the substituent.

Table 11. Heats of polymerisation and the capacities for polymerisation of substituted lactams.

No. of ring units n	Lactam*	$-\Delta H$, kcal mole⁻¹	References	Capacity for polymerisation	Initiator	References
5	α-pyrrolidinone	1.3	32	+	water, alkali	50,103,113
	1-methyl	0.8	112	—	alkali	113
	5-methyl-	—	—	—	water, alkali	113
	4-carboxy-	—	—	+	—	114
	N-methyl-	0 8	33,112	—	water, acid, alkali	33,52
6	α-Piperidinone	1.1	32	+	alkali	52,53,103
	1-methyl-	—	—	—	alkali	113
	N-methyl-	—0.5	33,112	—	alkali	113
7	ε-Caprolactam	3.3	38	+	water, acid, alkali	50,79,103
	1-methyl-	2.3	112	+	water, alkali	112,113
	5-methyl-	3.8	33	+	6,6 salt**	52
	7-methyl-	3.8	33	+	6,6 salt**	52
	7-ethyl-	4.5	115	+	water, acid	115
	7-propyl-	3.4	115	+	water, acid	115
	5-n-heptyl-	—	—	—	6,6 salt**, water	116
	5-phenyl-	—	—	—	water	113
	1,1-dimethyl-	4.8	117	+	water, alkali	117
	N-methyl-	2.3	33,112	—	water, alkali	48,123
8	ξ-Oenantholactam	5.4	38	+	water, alkali	52,85
	1-methyl-	3.9	33,112	+	water, alkali	52,113
	8-ethyl-	6.8	115	+	water, acid	115
	8-propyl-	4.9	115	+	water, acid	115
	N-methyl-	3 9	33,112	+	water	52,123
9	η-Caprylolactam	7.8	34	+	water, acid, alkali	34,79,118
	N-methyl-	—	—	+	water, alkali	118
	N-n-butyl-	—	—	+	water, alkali	118
13	Laurolactam	1.5	41,42	+	water, acid, alkali	42,118
	N-methyl-	—	—	+	water, alkali	118
	N-n-butyl-	—	—	+	water, alkali	118

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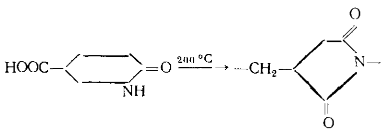
* The authors begin the numbering of the ring positions from the heteroatom.

** The 6,6 salt is hexamethylenediammonium adipate.

Thus one may conclude that the entropy and enthalpy effects of the substituent make the free energy of cyclisation of the lactam more negative compared with the unsubstituted analogue, as a result of which the equilibrium is displaced towards the cyclic compound.

The ready conversion of 4-carboxy-α-pyrrolidinone into a polyamide on heating above the melting point of the monomer, described by Klein and Reimschuessel[114], constitutes an appreciable deviation from the usual behaviour of substituted cyclic carbonyl monomers:



Such capacity for polymerisation can in all probability be accounted for by the reactivity of the substituent in the lactam, the latter isomerising to a cyclic imide on heating.

Seven- and eight-membered rings. While the heats of polymerisation of *C*-substituted five- and six-membered lactams are lower than those of the corresponding unsubstituted analogues, ΔH for substituted seven- and eight-membered lactams may be both greater and smaller than the enthalpies for the corresponding unsubstituted cyclic amides. Since the entropies of polymerisation of the above compounds are not available, one can only suppose that in this instance the thermodynamic characteristics of the substituent promote the cyclisation reaction, displacing the polymer $\rightleftharpoons$ monomer equilibrium towards the monomer. This is confirmed by the concentrations found in the polymerisation of substituted lactams with seven- and eight-membered rings (Table 12).

Table 12. The equilibrium concentrations of the monomer in the polymerisation of seven- and eight-membered lactams[52].

Lactam*	Content of lactam at equilibrium, wt.%	*T*, °C	Initiator, %
ε-Caprolactam	7	260	6,6 salt, 5
5-methyl-	8.8	254	6,6 salt, 10
7-methyl-	9.5	254	6,6 salt, 7
4-methyl + 6-methyl isomers	12.2	254	6,6 salt, 5
5-ethyl-	30.2	254	6,6 salt, 10
5-n-propyl-	41	254	6,6 salt, 10
5-isopropyl-	37	254	6,6 salt, 20
5-t-butyl-	74	254	6,6 salt, 20
5-cyclohexyl-	50	254	6,6 salt, 20
ξ-Oenantholactam	0	260	water, 4
8-ethyl-	3	260	water, 2
8-n-propyl-	6	260	water, 2
N-methyl-	20	260	water, 2

* The authors begin the numbering of the ring positions from the heteroatom.

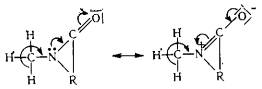
The data in Table 12 show that the introduction of a substituent into the lactam ring leads to an increase of the equilibrium concentration of the monomer in the monomer–polymer system, the influence of the substituent on the lactam polymerisation process being greater the greater the bulk of the substituent.

(9–13)-Membered Rings. There are contradictory data concerning the influence of the substituent on the formation of nine-membered lactam rings[121,122]. However, according to the available results for the polymerisation of various lactams, the influence of substituents on the capacity of lactams for polymerisation is smaller the larger the ring.

2. *N*-Substituted Lactams

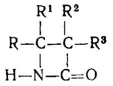
It is seen from Table 11 that the strain in the rings of *N*-substituted lactams is much smaller than in the rings of the unsubstituted lactams and their capacity for polymerisation is correspondingly smaller[112]. Data are available for the capacities for polymerisation of *N*-methyl-ζ-oenantholactam[111] and the *N*-methyl derivative of the lactam of lauric acid[118]. The polymerisation of *N*-methyl-ε-caprolactam has been investigated by many workers[48,53,106,168] under the conditions of both hydrolytic and anionic polymerisation. The possibility of the polymerisation of *N*-methyl-ε-caprolactam, suggested in one of the investigations[124], has been the subject of much doubt[48,53,110,111]. The capacity of *N*-acetoacetyl-ε-caprolactam for anionic polymerisation has also been studied[125] and it has been found that the *N*-acetoacetyl-substituted lactam not only does not undergo polymerisation but actually inhibits the polymerisation of ε-caprolactam.

Prochaska[108] suggested that a necessary condition for the polymerisation of lactams is the presence of a hydrogen atom in the amide group. This view is supported by Jumoto[107] and Hall[113]. On the basis of infrared spectroscopic data for five-, six-, and seven-membered lactams, Ogata[49] concluded that the absence of capacity for polymerisation is a common property of all *N*-substituted lactams. He believes[49] that this is caused by the high stability of such cyclic compounds due to the increase of the resonance effect in the amide group as a result of *N*-substitution and not due to the absence of a hydrogen atom:



The increase of the resonance stabilisation of *N*-substituted lactams owing to the inductive effect of the alkyl groups should lead to an increase of the dipole moment of the molecule. In fact, according to Ogata[110], the dipole moment of *N*-methyl-ε-caprolactam is 4.23 (cf. $\mu = 3.89$ for ε-caprolactam, Table 7). The capacity for polymerisation of *N*-substituted (8–13)-membered lactams indicates a decrease of the influence of the substituent with increase of ring size.[52]

It has been found that even the most reactive four-membered substituted cyclic β-lactams having the general formula



$$\begin{array}{c} \quad R^1\ R^2 \\ R{-}\overset{|}{C}{-}\overset{|}{C}{-}R^3 \\ H{-}\underset{|}{N}{-}\underset{|}{C}{=}O \end{array},$$

where R=H, alkyl, aryl, alkylaryl, or arylalkyl and R^1, R^2, and R^3 = H, CH_3, or C_2H_5, show a decrease of the tendency towards polymerisation with increase of the degree of substitution[126].

Thus examination of the influence of substituents on the reactivity of lactams shows that the following postulates may be regarded as proved.

1. The substituent reduces the reactivity of lactams.
2. The influence of the substituent is greater the smaller the size of the lactam ring.
3. An increase in the size of the substituent in the lactam ring also results in a decrease of the reactivity of the cyclic amide.
4. The reactivity of lactams depends on the position of the substituent in the ring.

It is apparently possible to arrange systematically data for the polymerisation of substituted lactams in terms of the ease of formation of the cyclic monomer. Two factors operate in cyclisation. The first is the enthalpy effect, the magnitude of which is a function of ring size and the presence of substituents. The second is the ease with which groups at the end of the chain can approach one another to a distance necessary for cyclisation, namely the entropy effect. The probability of cyclisation diminishes with increase in chain length, which evidently leads to a decrease of the entropy of cyclisation.

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The Mechanisms of the Stabilisation of Thermostable Polymers

O.A.Shustova and G.P.Gladyshev

New data on the stabilisation of thermostable polymers are presented, attention being concentrated on quantitative data and reaction mechanisms. The theoretically feasible polymer stabilisation pathways at temperatures exceeding 250°C are briefly analysed, various methods for the inhibition of thermo-oxidative and thermal degradation of polymer systems are considered, and experimental results concerning the kinetics and mechanisms of these processes are described.

One of the general polymer stabilisation pathways, based on non-chain inhibition reactions, is analysed in detail; procedures for the generation of highly active stabilisers directly in polymeric materials or during their processing and employment are considered, new approaches are proposed to the solution of the problem of the stabilisation of thermostable polymers, and certain experimental data are quoted.

The bibliography includes 203 references.

CONTENTS

I. INTRODUCTION

Studies on the stabilisation of thermostable polymers constitute an independent branch of the science of the ageing of polymers, since in this field one cannot use the general procedures which have become common in the stabilisation of non-thermostable polymer materials. The considerable interest in the problem of the stabilisation of thermostable polymers is indicated by the abundance of monographs, reviews, and experimental studies on this problem[1-44] published in recent years. Unfortunately, most of these are concerned solely with the influence of particular additives on the ageing of polymers or with the problem of stabilisation when the usual antioxidants and inhibitors of thermal degradation, effective at temperatures not exceeding 200–250°C, are used.

Among highly thermostable polymers[†], organosilicon, organofluorine, and other polymers derived from organic derivatives of the elements, phenyl ether resins, polyimides, etc. are of greatest interest[45,46]. The available literature information about the mechanisms of the stabilisation of these polymers is contradictory[28,45-58]. In a number of studies, conclusions have been reached without taking into account the experimental conditions. For example, some workers investigated the relevant processes under conditions where the rate of the latter is limited by the diffusion of oxygen or of the degradation products and yet this factor was not taken into account in the determination of the mechanism.

The most interesting studies dealt with the stabilisation of polymeric liquids[55-57], but the conclusions reached in such investigations concerning the process mechanisms cannot always be extended to solid polymeric systems[59,60].

Several general approaches have been formulated in recent years and new mechanisms of the stabilisation of thermostable polymers have been proposed[4,19,20,35-38]. Although the theory of high-temperature stabilisation is not complete and only a few theoretical studies have been made as yet, important data have accumulated and can be usefully considered.

This review deals with the mechanisms of the stabilisation of thermostable polymers which are experimentally and theoretically justified and also with certain empirical data taken from studies on the stabilisation of thermostable polymers published in 1969–1975. Studies which are of practical interest alone, the references to which may be found in a number of monographs[5-7,14,15,17,18,43] and reviews[21,29,31,32-35], are not discussed.

II. GENERAL APPROACHES TO THE PROBLEM OF THE STABILISATION OF POLYMERS

It has come to be assumed that polymers may be stabilised in two ways: by the introduction of special additives (stabilisers) or by modification using different procedures. The first method is most widely used. Stabilisers are normally involved in the following reactions:

1. Interaction with free radicals leading to the deactivation of active centres and chain termination.
2. Interaction with the molecular degradation products involved in [further] reactions and leading to the decomposition of the polymer.
3. Interaction with active agents penetrating the polymer from an external medium[4,37].
4. The blocking (deactivation) of the reactive centres of macromolecules (weak bonds).
5. Deactivation of impurities by the binding of the latter into stable complexes.

[†] Polymers which can be used at temperatures above 200–250°C will henceforth be referred to for brevity as thermostable.

From the thermodynamic standpoint, the hypothesis that the chemical reactions leading to stabilisation should result in the formation of stronger bonds compared with those whose presence in the polymer is responsible for its thermodynamic instability under the given conditions is frequently valid[4]. It can be shown that this principle holds also from the kinetic standpoint, since the chemical bond energy is both a thermodynamic and a kinetic criterion of the occurrence of bond dissociation processes under the influence of heat and chemical agents. Knowing the detailed polymer decomposition mechanism, one can therefore select stabilisers for thermostable polymers on the basis of the chemical bond strengths.

Inhibited processes can be divided into two groups: those involving chain and non-chain inhibition[19,20]. Chain inhibition presupposes the deactivation of the active centres for the chain process, i.e. their conversion into inactive products from the standpoint of chain propagation. Non-chain inhibition is associated with the deactivation of a substance involved in any reactions leading to the degradation of the polymer. In chain polymer degradation processes, non-chain inhibition is associated with the deactivation of the substances initiating the chains or involved in the chain propagation reactions. In non-chain polymer degradation processes, non-chain inhibition presupposes the deactivation of the active centres responsible for the degradation.

Thus, there are two general ways of inhibiting the polymer degradation processes.

1. Inhibition of the chain processes by the introduction into the system of substances leading to chain termination.
2. The removal from the system of chemical agents (present in the polymer composition or formed as a result of ageing), weak bonds, etc.

A rigorous kinetic criterion of non-chain inhibition, associated with the deactivation of a particular compound, is a zero rate of initiation (reaction) with participation of the given substance X′ during the ageing of the polymer:

$$w_{X'} = 0$$

Quantitative criteria of the efficiency of non-chain inhibition can be readily obtained from the following ratios:

$$w_{Z+X'}/w,$$

where $w_{Z+X'}$ and w are the rates of the non-chain inhibition and the overall rate of the process in the absence of the stabiliser Z.

Chain processes are inhibited by inhibitors of thermal (thermostabilisers) or oxidative (antioxidants) degradation of polymers. The inhibition of the decomposition of the polymer is associated with chain termination, which can be represented by elementary reactions of the following type:

$$\mathrm{R^{\cdot} + InH \rightarrow RH + In^{\cdot}}$$
$$\mathrm{R^{\cdot} + In^{\cdot} \rightarrow RIn}$$
$$\mathrm{RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}}$$
$$\mathrm{RO_2^{\cdot} + In^{\cdot} \rightarrow} \text{ inactive products,}$$
$$\mathrm{2In^{\cdot} \rightarrow In - In}$$
$$\mathrm{R^{\cdot}, R_2^{\cdot} + X \rightarrow} \text{ inert products, etc.,}$$

where R˙ is the active radical propagating the chain, InH the inhibitor molecule, X a stable radical or molecule containing a short [multiple ?] bond, etc.

The assortment of stabilisers effective below 200–250°C is fairly extensive[5,14–18,27,31,61]. However, at higher temperatures the mechanism of the degradation of polymers changes and the "low-temperature" stabilisers such as phenols, amines, etc. frequently vaporise or are themselves converted into initiating agents. The assortment of suitable stabilisers under these conditions is therefore restricted. Inhibiting activity is shown at elevated temperatures by compounds such as certain phosphites[26,35], inorganic acids[62–66], alkalies[67,68], metals and their compounds[35,69–87], and polyconjugated systems[21,77].

Furthermore, at high temperatures the method involving the generation of radicals directly in polymer compositions is effective. Such acceptors must be themselves firmly stable and must not participate in chain initiation and chain transfer processes[4].

The procedures for the elimination of active degradation products have been used for a long time in polymer chemistry[5]. On the other hand, methods for the removal of weak bonds and other initiating components from systems have been inadequately studied. Although it has been known for a long time that oxygen acceptors inhibit oxidation, the lack of knowledge about the mechanism as a whole precluded the determination of the optimum conditions for the application of these substances, led to contradictory data, etc. This approach became very promising only after it had been shown theoretically[4,19,20,37,38] that the oxidative ageing of polymers can be fully suppressed by using appropriate oxygen acceptors. The essential feature of the elementary interaction of O_2 (as well as other agents causing the degradation of polymers) with the acceptor, called non-chain inhibition[19,20], is that, under conditions of a fairly high reactivity and concentration of the stabiliser Z, oxygen is not involved in initiation reactions of the type

$$\mathrm{RH + O_2 \rightarrow R^{\cdot} + HOO^{\cdot}}$$
$$\mathrm{2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2}\text{ ,etc.}$$

and is fully absorbed in the reaction with the stabiliser:

$$nZ + \frac{m}{2}O_2 \rightarrow Z_nO_m \text{ (inert product).}$$

Table 1. Schematic description of polymer stabilisation pathways.

Type of initiation of degradation	Stabilisation method	Substances involved in reactions (examples)
1. Dissociation of main macromolecular chains, scission of side (terminal) groups: $R_m{-}R_n \rightarrow R_m^{\cdot} + R_n^{\cdot}$ $R_m{-}YX_2{-}R_n \rightarrow R_m{-}YX{-}R_n + \dot{X}$	(a) chain inhibition: $R^{\cdot} + YR' \rightarrow RY + R^{\cdot}$ $R' \longrightarrow R'R$ $R^{\cdot} + Z'^{\cdot} \rightarrow RZ'$ R′R and RZ′ are inert products.	YR′-InH-antioxidant, thermostabiliser; Z′˙—stable radical
	(b) non-chain inhibition, structural stabilisation	substances forming clathrate compounds
2. Reactions with chemical agents: $R_m{-}YX_2{-}R_n \xrightarrow{X'} R_m{-}Y\dot{X}{-}R_n + X'X^{\cdot}$ (or active ionic forms)	(a) chain inhibition: $R'^{\cdot} + Z'^{\cdot} \rightarrow$ inert products (b) non-chain inhibition: $X' + Z \rightarrow$ inert product	Z′˙—radical acceptor; X′—chemical agent (O_2, O_3, H_2O, HCl, etc.) Z—acceptor X′ (metal, metal oxide, sulphide, etc.)
3. Reaction of weak bonds and active impurity groups: $R_m{-}Y{-}Y{-}R_n \rightarrow R_mY^{\cdot} + R_nY^{\cdot}$ $R_m{-}X_1{-}R_n \xrightarrow{Y_2} R'^{\cdot}$ + products (where $X_1 = {>}C{=}C{<}$, $-C{\equiv}C$, etc.)	(a) chain inhibition: $R'^{\cdot} + Z' \rightarrow$ inert products (b) non-chain inhibition: $R_m{-}X_1{-}R_n \xrightarrow{Z_1}$ inert product $Y_2 + Z_2 \rightarrow$ inert product	Z′—stabiliser (InH, stable radical) Z_1-chemical agent (H_2, F_2, etc.); Z_2—acceptor of chemical agent; Y_2—chemical agent

The employment of non-chain inhibition in combination with the generation of highly active oxygen acceptors directly in polymeric systems made it possible to increase significantly the lifetime of certain thermostable materials[4,37,38]. A number of chemical processes permitting the generation of highly active stabilisers of different types[37,75] in polymer compositions virtually in any specified temperature range have been proposed recently (Section IV). Thus the non-chain inhibition method has been extended to various types of ageing.

Table 1 summarises the possible polymer stabilisation pathways. The methods listed in Table 1 are applicable to the stabilisation of not only thermostable, but, in principle, any polymers undergoing decomposition via different mechanisms.

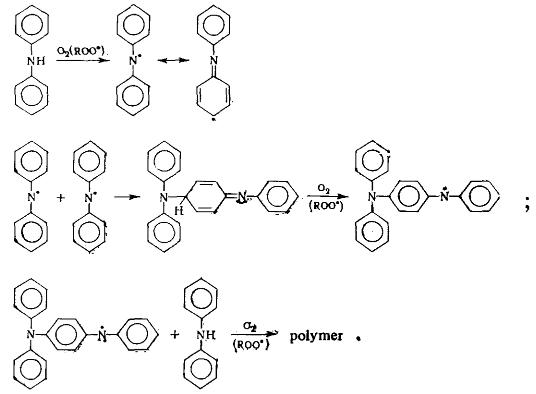
Methods for increasing the stability of polymers based on their modification[1,16,88-95] and structural stabilisation[19,96-98] and the structural-chemical stabilisation of chemical agents and stabiliers[4,19], etc. are also known. These procedures, involving the employment of the cage effect[45,99-101], the reduction of the rate of diffusion of active agents in polymers[5,102,103], etc. are not considered in detail in the present review. Special stabilisation methods[104,105] used in light- and radiation-induced ageing processes[1,106,107] are not analysed either.

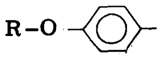
III. THE MECHANISMS OF THE STABILISATION OF THERMOSTABLE POLYMERS

As already stated above, a number of inhibiting systems retarding the chain degradation of polymers at elevated temperatures are known. Stabilisation methods can be based on both chain and non-chain inhibition procedures. Since the stabilisation of many polymer compositions involves the application of both these procedures, it is useful to consider the mechanisms of the inhibition of degradation on the basis of the nature of the stabiliser.

Berlin, who investigated the inhibiting properties of various polyconjugated systems, showed that they are frequently effective inhibitors of high-temperature chain processes[21,77].

Many polyconjugated systems, including those formed in consequence of chemical transformations of antioxidants and substrates, exhibit a high inhibiting activity. Thus, polydiphenylamines, with a higher inhibiting activity than the initial amines, are formed in the oxidative dehydropolymerisation of secondary aromatic amines[21]. One of the hypothetical mechanisms of the formation of these polymers may be as follows:



Stemniski et al.[84] pointed out the possibility of inhibiting the thermal degradation of polyphenyl ethers at 420–440°C and their thermo-oxidative degradation at 250–300°C by organic derivatives of variable-valence metals (Co, Cu, Ti, Al, Mn, Ni, Fe, Be, and Cr) and proposed a mechanism for their action. Thus they showed that the decomposition of a polyether involves, on the one hand, the formation of relatively stable free radicals of the type  or their derivatives. On the other hand, variable-valence metal compounds interact with hydroperoxides in the following way:

$$M^{2+} + ROOH \rightarrow M(\dot{O}H)^{2+} + RO^{\cdot} \quad ,$$
$$M(\dot{O}H)^{2+} + ROOH \rightarrow M^{2+} + HOH + ROO^{\cdot} \quad .$$

Archer and Bozer[87] suggest that the stabilisation of polyphenyl ethers by organic cobalt salts is associated with the interaction of the metal ions and active radicals:

$$Co^{3+} + R^{\cdot} \rightarrow Co^{2+} + R^{+} \quad . \tag{1}$$

One may postulate that analogous processes occur also in the reactions of RO•, ROO•, etc. radicals. There is reason to believe[57] that the efficiency of reaction (1) is not very high when inorganic salts are used.

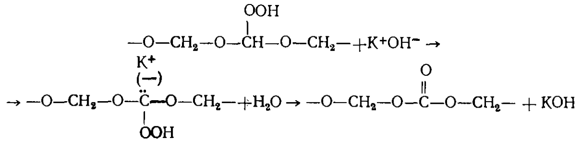
According to Ravner et al.[57], the high-temperature stabilisation in the presence of alkalies, for example KOH, is associated with the occurrence of the following reactions:

$$\text{I.}\quad ROO^{\cdot} + KOH \rightarrow ROH + KOO^{\cdot} \quad ,$$
$$KOO^{\cdot} + R'O^{\cdot} \rightarrow KOR' + {}^{\cdot}OO^{\cdot}\,(=O_2) \quad ,$$
$$KOR' + H_2O \rightarrow KOH + R'OH \quad ,$$
$$\text{II.}\quad 4\,KOH + 3O_2 \rightarrow 4\,KOO. + 2H_2O \quad ;$$
$$KOO^{\cdot} + ROO^{\cdot} \rightarrow KOOR + O_2 \quad ,$$
$$KOOR + R'O^{\cdot} \rightarrow ROR' + KOO^{\cdot} \quad .$$

Peroxides of the type ROOM can be generated similarly from basic salts of other alkali metals. However, the details of this interesting mechanism require experimental tests.

The stabilisation probably involves mechanism (I) when the decomposition of peroxy-radicals is base-catalysed; in other cases, mechanism (II) may obtain. It is noteworthy that there is a correlation between the stabilising activity of alkali metal [and alkaline earth] hydroxides and the ability of the alkali metals to form peroxides; calcium and strontium hydroxides are exceptions.

Alkali metal hydroxides are also effective stabilisers of trioxan–dioxolan copolymers[48]. It is suggested that alkalies decompose hydroperoxides without breaking macromolecular bonds. Thus the secondary hydroperoxy-groups present in the polymer can react with KOH via the following mechanism:



$$-O-CH_2-O-\underset{}{\overset{OOH}{\overset{|}{C}H}}-O-CH_2- + K^{+}OH^{-} \rightarrow$$
$$\rightarrow -O-CH_2-O-\underset{\underset{OOH}{|}}{\overset{K^{+}\,(-)}{\ddot{C}}}-O-CH_2- + H_2O \rightarrow -O-CH_2-O-\overset{O}{\overset{\|}{C}}-O-CH_2- + KOH \quad .$$

It is noteworthy that an inhibiting activity of KOH is observed at comparatively low temperatures in the thermal decomposition of polyethylene[67,68]. This involves a decrease of the branching of the polymer, lowers the concentration of "weak" sites in the macromolecules, and prevents the formation of fragments with unsaturated terminal groups[68].

Nielsen[55,56] used iron and cerium compounds as stabilisers in the study of the oxidation of liquid siloxanes. It was found that below 150°C iron(III) compounds accelerate the thermo-oxidative degradation. At higher temperatures the same compounds have a stabilising effect, a definite Fe³⁺ concentration, ensuring the minimum rate of oxidation, corresponding to each temperature. The author believes that the following reactions occur in the degradation of liquid siloxanes.

Initiation:

$$\equiv SiCH_3 + O_2 \rightarrow \equiv SiCH_2 + {}^{\cdot}OOH \text{ and (or)}$$
$$\equiv SiCH_3 + O_2 \rightarrow [\equiv SiCH_2OOH] \rightarrow \equiv Si^{\cdot} + {}^{\cdot}OH + CH_2O \quad .$$

Chain propagation:

$$\equiv SiCH_2^{\cdot} + O_2 \rightarrow \equiv SiCH_2OO^{\cdot} \quad ;$$
$$\equiv SiCH_2OO^{\cdot} \rightarrow \equiv SiO^{\cdot} + CH_2O \quad ;$$
$$\equiv SiO^{\cdot} + O_2 \rightarrow \equiv SiOO^{\cdot} + O \quad ;$$
$$\equiv SiCH_3 + \equiv SiO^{\cdot} \rightarrow \equiv SiOH + \equiv SiCH_2^{\cdot} \quad .$$

Chain branching:

$$\equiv SiCH_2OOH \rightarrow \equiv Si^{\cdot} + {}^{\cdot}OH + CH_2O \quad ;$$
$$\equiv SiOOH \rightarrow \equiv SiO^{\cdot} + {}^{\cdot}OH \text{ or } \equiv Si^{\cdot} + {}^{\cdot}OOH \quad ;$$
$$HOOH \rightarrow 2{}^{\cdot}OH \quad ;$$
$$CH_2O + O_2 \rightarrow {}^{\cdot}CHO + {}^{\cdot}OOH \quad .$$

Chain termination:

$$\equiv Si^{\cdot} + {}^{\cdot}OH \rightarrow \equiv SiOH \quad ;$$
$$\equiv Si^{\cdot} + {}^{\cdot}OSi\equiv \rightarrow \equiv Si{-}O{-}Si\equiv \quad ,$$

etc.

It is suggested that free radicals are destroyed as a result of the reduction of the metal ion:

$$M^{x+1} + {}^{\cdot}R \rightarrow M^{x} + R^{+} \text{ (where } R^{\cdot} \equiv Si^{\cdot} \text{ or } \equiv SiCH_2^{\cdot}) \quad , \qquad (2)$$

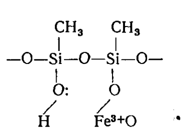
and that at a fairly high oxygen concentration there is a possibility of the regeneration of the metal ion M^{X+1} via the reaction

$$M^{x} + O_2 \rightarrow M^{x+1} + O_2^{-} \quad . \qquad (3)$$

Further studies[56] suggested also the occurrence of non-radical processes of the type $\equiv SiCH_3 + Fe^{3+}O$ complex $\rightarrow \equiv SiOH + Fe^{2+}$ complex followed by oxidation of the product and regeneration of the initial compound:

$$Fe^{2+} \text{ complex} + O_2 \rightarrow Fe^{3+}O \text{ complex.}$$

It is suggested that the stabilisation of liquid dimethylsiloxane by iron octoate [octanoate ?] involves the formation of a chelate structure of the type



There have been a number of other studies on stabilisation in the presence of metal ions. However, the majority of the results refer to low temperatures. Nevertheless, some of them are important in the consideration of high-temperature processes. We may mention a study[74] where the influence of variable-valence metals on the resistance of polyurethanes to thermo-oxidation was investigated. It was shown that, when the system contains hydroperoxides (120°C), its stabilisation is associated with the following reactions:

$$ROOH + M^{2+} \rightarrow M^{3+} + OH^{-} + RO^{\cdot} \quad ;$$
$$ROOH + M^{3+} \rightarrow RO_2^{\cdot} + H^{+} + M^{2+} \quad .$$

Presumably the oxidation of certain thermostable polymers at temperatures not exceeding 200–250°C in the presence of complex inhibitors can be described in terms of the scheme for the inhibited oxidation of hydrocarbons[74,108,109]:

$$\gamma \rightarrow r^{\cdot} \quad ;$$
$$r^{\cdot} + \text{polymer} + O_2 \xrightarrow{w_i} RO_2^{\cdot} \quad ;$$
$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{\eta k_6} \text{products} + h\nu \quad ;$$
$$MA_2 + L \overset{K_p}{\rightleftarrows} ML \quad ;$$
$$RO_2^{\cdot} + ML \xrightarrow{k_7} \text{inactive product} \quad ;$$
$$RO_2^{\cdot} + L \xrightarrow{k_7'} \text{inactive product} \quad ,$$

where γ is the initiator decomposing at a rate w_i, $r^{\cdot}$ the radical initiator, L the ligand (for example urethane) molecule, MA_2 the variable-valence metal salt, ML the molecule of the complex, η the overall chemiluminescence yield, and the constants k with the appropriate subscripts are the rate constants for the elementary reactions.

When the concentration of peroxy-radicals corresponds to a steady state and $[M] \gg [L]$, the following expression holds:

$$\frac{I_0 - I}{\sqrt{I_0 I}} = \frac{[MA_2]_0}{\sqrt{w_i k_6}} \left[\frac{k_7 \cdot K_p [L]_0}{1 + K_p [MA_2]_0} + k_7 \right] \quad , \qquad (4)$$

where I_0 and I are the initial and final intensities of illumination and K_p is the equilibrium constant. Eqn. (4) holds satisfactorily in many instances, which confirms the above stabilisation mechanism.

It has been noted[42] that, at temperatures of the order of 350°C and above, the mechanism of the stabilisation of polyorganosiloxanes in the presence of metal-phthalocyanines can be attributed not only to the interaction of the paramagnetic species with the radicals but also to trans-coordination accompanied by the formation of complicated chelate compounds.

The stabilising action of metals and their oxides at high temperatures is attributed by some workers[42,47,51,75,86] to the orienting effect of the dispersed particles, which serve as centres for the formation of secondary structures, or to the formation on degradation of new polymers with metal heteroatoms in the chain. These mechanisms do indeed occur, but they are not always decisive. There is no doubt that in a number of cases the stabilising action of many metals at high temperatures is largely associated with a non-chain inhibition reaction or with oxidation–reduction processes.

Analysis of a number of studies[29,51,56,74,75] has shown that the influence of metals and many inorganic compounds on the ageing of polymers cannot always be accounted for unambiguously. Thus it has been stated that iron and tin[74] salts, aluminium, chromium, zinc, phosphorus, and boron[76] oxides, and metallic lead and cadmium[51] accelerate the oxidation process under certain conditions. On the other hand, it has been noted in other investigations[5,75] that these compound have an inhibiting effect. Cobalt, copper, and cerium[74] salts and iron, magnesium, and other oxides[80] usually stabilise thermostable materials at temperatures in the range 300–390°C; at low temperatures or at 400°C and above, they do not inhibit or actually accelerate polymer decomposition processes[56,76,80]. Many apparent contradictions in the interpretation of the action of a wide variety of stabilisers used in the high-temperature ageing of polymers can be readily explained by taking into account the conditions under which the studies were carried out and also the characteristics of the methods, which are sometimes imperfect.

Examination of Table 1 in the preceding section shows that the use of non-chain inhibition processes leads to new possibilities for the solution of the problem of the stabilisation of thermostable polymers. This approach attracted the attention of investigators only in recent years[36,110-112] after the determination of the mechanism of stabilisation in the presence of oxygen acceptors, generated in polymer compositions or articles[4,19,20,38,113]. Subsequently Shustova showed that the application of a non-chain inhibition method can be sometimes effective in the stabilisation of thermostable materials, losing many of their useful properties under the influence of various chemical agents[37,111,186].

We shall now examine the characteristics of the mechanism of non-chain inhibition[4,37,112,114]. The oxygen acceptors generated in polymer compositions or acceptors introduced into the polymer during its processing may serve as highly effective inhibitors, preventing oxidative degradation via a non-chain inhibition mechanism. Acceptors of the first group exhibit a high activity already at room temperature and for technical reasons cannot therefore be introduced in the usual way. On the other hand, acceptors of the second type exhibit a low activity under these conditions, but become fairly effective at high temperatures.

We shall now consider the general kinetic scheme (A) for the oxidative degradation of polymers containing mobile hydrogen atoms involved in initiation processes[4,20].

I. Initiation:

$$\begin{array}{ll}
\text{weak bond} \xrightarrow{k_{\text{in}}} 2\dot{R}_{\text{pri}}\ ; & \text{(a)}\\
\dot{R}_{\text{pri}} + RH \xrightarrow{k'_{\text{in}}} R^{\cdot} + R_{\text{pri}}H\ ; & \text{(b)}\\
RH + O_2 \xrightarrow{k_0} R^{\cdot} + H\dot{O}_2\ ; & \text{(c)}\\
2RH + O_2 \xrightarrow{k'_0} 2R^{\cdot} + H_2O_2\ . & \text{(d)}
\end{array} \qquad \text{(A)}$$

II. Chain propagation:

$$R^{\cdot} + O_2 \xrightarrow{k_1} R\dot{O}_2 \quad ; \qquad \text{(a)}$$

$$\begin{array}{l}
R\dot{O}_2 + RH \xrightarrow{k_2} R^{\cdot} + ROOH \xrightarrow{k_3} \text{inert products;}\\
\quad\text{branching} \downarrow k_3\\
\quad\quad \text{products} \rightarrow 2R'^{\cdot} \quad .
\end{array} \qquad \text{(b)}$$

III. Chain termination:

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_4} R{-}R$$

$$R\dot{O}_2 + R^{\cdot} \xrightarrow{k_5} ROOR$$

$$R\dot{O}_2 + R\dot{O}_2 \xrightarrow{k_6} \text{products.}$$

IV. Non-chain inhibition:

$$Z + O_2 \xrightarrow{k_2} \text{inert products.}$$

If k_Z is fairly high, it is possible to select conditions such that the oxygen reacts virtually only with Z and is not involved in other elementary reactions.

On the basis of published data[109,115,116], we shall adopt the following rate constants for the elementary reactions (Ic), (Id), and (IIa) and the concentrations of the components (250–350°C):

$$k_0 = 10^{-2} - 1 \text{ litre mole}^{-1}\,\text{s}^{-1};\ k'_0 = 10^{-3} - 10^{-1} \text{ litre}^2\,\text{mole}^{-2}\,\text{s}^{-1};$$

$$k_1 = 10^8 \text{ litre mole}^{-1}\,\text{s}^{-1}$$

$$[RH] = 10 \text{ M} \quad ; \quad [O_2] = 10^{-4} \text{ M} \quad ;$$

$$[R^{\cdot}] = 10^{-8} - 10^{-7} \text{ M} \quad .$$

The rates of the corresponding elementary processes involving oxygen are:

$$w_{RH+O_2} = k_0[RH]\cdot[O_2] = 10^{-5} - 10^{-3} \text{ mole litre}^{-1}\,\text{s}^{-1};$$

$$w_{2RH+O_2} = k'_0[RH]^2\cdot[O_2] = 10^{-5} - 10^{-3} \text{ mole litre}^{-1}\,\text{s}^{-1};$$

$$w_{R^{\cdot}+O_2} = k_1[R^{\cdot}]\cdot[O_2] = 10^{-4} - 10^{-3} \text{ mole litre}^{-1}\,\text{s}^{-1}.$$

Next we assume that $w_{Z+O_2} = 10^{-2}$ mole litre^{-1} s^{-1}. After recalculation for a heterogeneous process, these values correspond to the real case of the stabilisation at 350°C of siloxane elastomers by pyrophoric iron generated in the polymer on decomposition of iron oxalate[37,113] (iron concentration 5 wt.%; surface area $S \simeq 10$ m^2 g^{-1}; oxidation rate constant $k_{Fe} = 10^{-14}$ g^2 cm^{-4} s^{-1}).

Thus we have the following relation for a number of systems:

$$w_{Z+O_2} \gg w_{R^{\cdot}+O_2},\ w_{RH+O_2},\ w_{2RH+O_2}.$$

Bearing in mind that the equilibrium concentration of O_2 in polymers is low, it can be easily shown that, as long as Z does not react with oxygen, reactions (Ic), (Id), and (IIa) hardly play an appreciable role.

It is noteworthy that the above estimate is based on unduly low values of S and k_{Fe}. In real systems, it is possible to obtain pyrophoric metals with surface areas of 100 m^2 g^{-1} and more[117,118]. Furthermore, the oxidation rate constant may be greater than 10^{-14} g^2 cm^{-4} s^{-1}. Thus, in the presence of copper 350–400°C, we have $k \simeq 10^{-8}$ g^2 cm^{-4} s^{-1} and the rate of the reaction $Cu + O_2 \rightarrow Cu_2O \xrightarrow{O_2} CuO$ should reach 10^2 mole litre^{-1} s^{-1}.

When the mechanism of the oxidative degradation of polymers is known, it is easy to obtain quantitative criteria of the efficiency of the stabilisers Z. Thus, at low temperatures, when the oxidation of the polymer[109] proceeds in accordance with the classical mechanism A, one can usefully consider three cases.

If the oxygen concentration in the polymer is low and the reaction rate $-d[O_2]/dt$ is directly proportional to the oxygen pressure p_{O_2}, effective inhibition is observed when the following condition is fulfilled:

$$fk'_Z[Z] \gg \frac{k_1 w_{\text{in}}^{1/2}}{k_4^{1/2}},$$

where f is the number of oxygen molecules interacting with one stabiliser molecule ($fk'_Z \equiv k_Z$) and w_{in} is the rate of initiation.

At a high oxygen concentration in the polymer, when the rate of oxidation is independent of p_{O_2}, effective inhibition should be observed provided that

$$fk'_Z[Z] \gg \frac{k_2 w_{\text{in}}^{1/2}}{k_6^{1/2}}\,\frac{[RH]}{[O_2]}.$$

In the intermediate case, where chain termination in the absence of stabilisers proceeds via reactions (4)–(6), effective inhibition requires that

$$fk'_Z[Z] \gg \frac{k_2 w_{\text{in}}^{1/2}}{k_6^{1/2}}\,\frac{[RH]}{[O_2]}\,\gamma,$$

where

$$\gamma = f([O_2], [RH]).$$

As oxygen diffuses into the specimen, the stabiliser Z is consumed via reaction (IV), while the lifetime of the article is determined by the rate of diffusion of oxygen. Calculations have shown[4] that, even for polymers whose oxygen permeability coefficients are high and amount to approximately 10^{-6} cm^3/cm^2/s.cm/atm [cm^2 s^{-1} atm^{-1} ?],[4,119-122] the lifetime of specimens 0.1–1 cm thick can reach many tens and hundreds of hours in the temperature range 300–400°C.

As an example, we shall consider the specific instance where the entire oxygen diffusing into the system interacts with the active stabiliser Z and the lifetime of the specimen is determined by the rate of diffusion of oxygen[37, 38]. We assume that the lifetime of the polymer τ is equal to the time during which the specimen decomposes to the extent of 80% ($t_{80\%}$). If the specimen is a plate, oxygen diffuses from both sides and the two fronts of the reaction

$$Z + O_2 \rightarrow \text{inert product}$$

move at right angles to the surfaces of the plate towards the centre (there is no countercurrent diffusion of Z).

The following equation holds in this case:

$$P = -D_{O_2}(\partial c/\partial x), \tag{5}$$

where P is the permeability (the amount of substance transferred per unit time, per unit area, and per unit thickness at the normal concentration or pressure difference), D_{O_2} the diffusion coefficient, and $\partial c/\partial x$ the concentration gradient. Next, one can write

$$P = D_{O_2}\frac{[O_2]_0 - [O_2]_x}{x}, \tag{6}$$

where $[O_2]_0$ is the concentration of oxygen at the interface (mole cm^{-3}) and $[O_2]_x$ the concentration in the specimen at a depth x.

Having denoted by w' the specific rate of reaction between Z and O_2 (equal to the number of moles of Z which have reacted per unit time and per unit area in the reaction zone), we obtain

$$w' = [Z]\frac{dx}{dt}, \tag{7}$$

where [Z] is the concentration of the substance (mole cm^{-3}), x the distance (cm), and t the time (s).

Since the rate of reaction (assuming that one mole O_2 reacts with one mole of Z) is equal to the flux of oxygen in the reaction zone and $[O_2]_0 \gg [O_2]_x$, one can write

$$w' = [Z]\frac{dx}{dt} = \frac{D_{O_2}[O_2]_0}{x}, \tag{8}$$

$$x\,dx = \frac{D_{O_2}[O_2]_0}{[Z]}\,dt. \tag{9}$$

Integration of Eqn. (9) yields

$$\frac{x^2}{2} = \frac{D_{O_2}[O_2]_0}{[Z]}t.$$

Thus the movement of the reaction front in the specimen is described by a parabolic law.

Next we obtain

$$t_{80\%} \equiv \tau = \frac{x^2}{2}\cdot\frac{[Z]}{D_{O_2}\cdot[O_2]_0} \simeq k_0\frac{l^2[Z]}{D_{O_2}[O_2]_0}, \tag{10}$$

where l is the thickness of the specimen and k is a coefficient equal to approximately 0.1 and determined by the stoichiometry of reaction (IV) and the assumptions made.

Taking into account the temperature variation of D_{O_2} and $[O_2]$, we have

$$\tau = \frac{kl^2[Z]}{D_0e^{-E_D/RT}\cdot\sigma_0'\cdot e^{-\Delta H/RT}},$$

where E_D is the activation energy for diffusion, ΔH the heat of solution of the gas, and D_0 and σ_0' are the corresponding pre-exponential factors.

However, ΔH is small for many polymers (between −2 and +2 kcal mole^{-1}), and one can therefore assume that

$$\tau = k\frac{l^2[Z]}{D_0e^{-E_0/RT}[O_2]_0}. \tag{11}$$

Since the diffusion coefficients in polymer compositions may be low, of the order of 10^{-8} and even 10^{-9} cm^2 s^{-1}, the lifetimes of polymeric materials can reach many thousands of hours.

Eqns. (10) and (11) have been obtained on the assumption that, in the absence of a stabiliser Z, the polymer decomposes almost at once. In the general case, the following expression is valid:

$$\tau = k\frac{l^2[Z]}{D_{O_2}[O_2]_0} + \tau' = k'l^2[Z] + \tau', \tag{12}$$

where τ' is a quantity comparable to the lifetime of the non-stabilised specimen.

Eqn. (12) has been obtained for the case where there is no diffusion of the stabiliser and the changes in the concentration of oxygen owing to its reaction with a polymer may be neglected. A detailed mathematical model without allowance for these limitations has been examined[39, 110] and it has proved possible to explain theoretically the causes of the appreciable deviations from Eqn. (12) for fairly large thicknesses of the polymeric specimens. It has also been shown that τ' may be set equal to the lifetime of the non-stabilised specimen only for highly efficient stabilisers such that $\tau' \ll \tau$. If the stabilisation effects are small, one must bear in mind that

$$\tau' = t_p + (2t_pt_D^{(1)}\alpha)^{1/2}.$$

where t_p is the polymer decomposition time subject to the condition that the concentration of oxygen is $[O_2]_0$ at all points in the polymer, $t_D^{(1)} = l^2/D_{O_2}$ is the time required by oxygen to diffuse into the specimen, and $\alpha = [Z]_0/\nu[O_2]_0$, ν being the stoichiometric coefficient of non-chain inhibition (the number of stabiliser molecules which have reacted with one oxygen molecule).

If the stabiliser Z inhibits not only oxidative but also thermol degradation and interacts with the primary radicals forming stable compounds of the type RZ (chain inhibition), then a simplified kinetic mechanism (B) of inhibited degradation is valid in the simplest instance:

$$\text{I.}\quad \text{weak bond} \xrightarrow{k_{in}} \dot{R}_{pri}\;;$$

$$\text{II.}\quad \dot{R}_{pri} + Z \xrightarrow{k_Z'} R_{pri}Z\;;$$

$$\text{III.}\quad O_2 + Z \xrightarrow{k_Z} \text{inert products.}$$

The mechanisms (A) and (B) described above do not take into account the possibility of chain-transfer processes via the stabiliser ($R_1R_2 + Z^{\cdot} \rightarrow R_1^{\cdot} + ZR_2$) and certain other elementary reactions. However, the satisfactory agreement of the calculations with the experimental results shows that the mechanism of the stabilisation processes considered here can operate[37, 38].

We shall now consider certain reactions of the type $Z + O_2 \rightarrow$ inert products which may be important for the stabilisation of polymers. It has been mentioned in the literature that the oxidation of organic compounds is inhibited by inorganic substances such as sulphides, phosphorus compounds, arsenic, antimony, bismuth, boron, silicon, tin, lead, sulphur, and others[123]. However, the mechanisms of these reactions have not been studied in detail and some of the above substances have not been used at all to stabilise polymeric materials[5].

Demonstration of the possibility of inhibition via a non-chain mechanism[4,37] necessitates the study of the rates of interaction of the above inhibitors with oxygen in order to find the optimum conditions for their utilisation as stabilisers. Together with classical data, quantitative studies published in recent years are considered below.

The kinetics of the oxidation of cobalt sulphide have been investigated[124] and it has been shown that, at temperatures of the order of 500°C, the process is described satisfactorily by the equation

$$\frac{d\alpha}{dt}=K(1-\alpha)^n,$$

where α is the degree of oxidation, $K = f(T, P_{O_2}, S_0)$ and n are constants, P_{O_2} is the oxygen pressure, and S_0 the surface area of the specimen.

It has been established[125] that Co_9S_8 is vigorously oxidised at 200°C with formation of the complex $Co_9S_8O_8$. The temperatures of the maximum rates of oxidation of the sulphides Sb_2S_3, AlFeS, FeS, Cu_3FeS_3, $CuFeS_2$, Fe_7S_8, MoS_2, ZnS, PbS, Cu_2S_3, CdS, and others, have been determined in a number of studies[126], and the reaction mechanisms have been established[127]. Thus it has been shown that chalcopyrite is oxidised via the mechanism

$$n\,CuFeS_2 + 4O_2 = 2\,FeO + Cu_2S\,(n-2)\,CuFeS_2 + 3SO_2 \quad ;$$
$$3\,FeO + \frac{1}{2}O_2 = Fe_3O_4 \quad ;$$
$$2\,Fe_3O_4 + \frac{1}{2}O_2 = 3\,Fe_2O_3,$$

and that the mechanism of the oxidation of iron and copper sulphides is[128]:

$$2\,FeS \xrightarrow{O_2} [2FeSO \xrightarrow{O_2} 2\,FeSO_2 \rightarrow Fe_2SO_3\cdot 2SO_2] \xrightarrow{-2SO_2} Fe_2O_3 \quad ;$$
$$Cu_2S \xrightarrow{O_2} [Cu_2SO \xrightarrow{O_2} Cu_2SO_2 \xrightarrow{O_2} Cu_2SO_3 \xrightarrow{-SO_2} Cu_2O\cdot SO_2] \xrightarrow{O_2} Cu_2O \rightarrow 2CuO \quad .$$

We may note that many sulphides are also effective synergistic agents, decomposing peroxides via a molecular mechanism[129,130]. Thus it has been shown[130] that WS_2 appreciably reduces the yield of radicals in the decomposition of hydroperoxides, while increasing its rate.

Antimony is slowly oxidised below 350°C, while at 500°C the process is rapid and involves the formation of Sb_2O_3 and then Sb_2O_4.[131] Vigorous oxidation of silicon and lead is observed above 400°C.[132-134]

The oxidation of a number of variable-valence metal hydroxides has been thoroughly studied, namely the oxidation of $Fe(OH)_2$, $Co(OH)_2$, $Mn(OH)_2$, etc. Manganese(II) hydroxide absorbs oxygen vigorously even at low temperatures[135]:

$$Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO_2 + H_2O \quad .$$

Certain variable-valence metal oxides are also effective oxygen acceptors[136-138]. For example, the kinetics of the oxidation of CoO in accordance with the equation

$$3\,CoO + \frac{1}{2}O_2 \rightarrow Co_3O_4$$

can be described by the equation

$$1-(1-\alpha)^{1/3} = kt \quad ,$$

where k is a constant.

Dithionites (for example sodium hyposulphite $Na_2S_2O_4$) can be used as oxygen absorbers. In the presence of alkalies, they readily interact with O_2 in the following way[132]:

$$S_2O_4^{2-} + 2OH^- + O_2 \xrightarrow{MOH} SO_4^{2-} + H_2O.$$

However, dithionites are as a rule unstable and decompose on heating:

$$2M_2^I\,S_2O_4 \xrightarrow{t^\circ > 100^\circ} M_2^IS_2O_3 + M_2SO_3 + SO_2.$$

The double salts of alkali metals and zinc dithionite ZnS_2O_4 are more stable.

Sulphites[139-141], pyrogallol mixed with alkalies[142-145], and other compounds[135,146,147] can sometimes serve as oxygen acceptors in model reactions.

Highly dispersed metals generated in polymers at high temperatures are active oxygen acceptors. Thus, copper with a high surface area absorbs oxygen even at low temperatures[148]. In the temperature range 400–500°C, the rate of the process is extremely high, but owing to the high dissociation pressure of CuO, oxygen cannot be removed completely from the system at these temperatures[135]. Metallic silver and silver on carriers (Al_2O_3, etc.) absorb O_2 at temperatures of 200–300°C; palladium catalyses the reaction of H_2 with O_2 at low temperatures, which proceeds rapidly and completely[149-151]. Finely dispersed iron reacts vigorously with oxygen even at low temperatures, forming oxides[117,149-152]. The thermodynamics of the oxidation of metals and various substances in the solid phase has been thoroughly studied[149-151]. Studies devoted to the thermodynamic aspects of the protection of highly thermostable materials against oxidation by the introduction of metals have also been made[153].

The kinetics of the oxidation of solids are frequently complex and, depending on their nature, the nature of the surface, and the thickness of the oxide film, are described by equations of different types[117,118,135,149-151,154,155]. For a constant concentration gradient of the component diffusing during oxidation, a parabolic law holds:

$$(\Delta l')^2 = 2k't \quad \text{or} \quad \left(\frac{\Delta m}{s}\right)^2 = k''t, \tag{13}$$

where l' is the thickness of the oxide layer (cm), k' a constant ($cm^3\ s^{-1}$), $\Delta m/s$ the increase in the weight of the oxide per unit area ($g\ cm^{-2}$), and k'' another constant ($g^2\ cm^{-4}\ s^{-1}$).

If the rate of oxidation is determined at interfaces, the following linear law holds:

$$\frac{\Delta m}{s} = k'''t, \tag{14}$$

where k''' is a constant ($g\ cm^{-2}\ s^{-1}$).

In a more complex case, where account must be taken of both laws, the following equation is frequently valid:

$$\frac{\Delta m}{s}\cdot\frac{1}{k'''} + \left(\frac{\Delta m}{s}\right)^2\frac{1}{k''} = t. \tag{15}$$

A cubic relation between $\Delta m/s$ and time is observed in the oxidation of very thin films or superdisperse metals:

$$\left(\frac{\Delta m}{s}\right)^3 = k_c''t \quad , \tag{16}$$

where k_c'' is a constant ($g^3\ cm^{-6}\ s^{-1}$); sometimes logarithmic or inverse logarithmic relations are valid:

$$\begin{aligned}\Delta l' &= k_1 - \text{const}\cdot\ln t,\\ \frac{1}{\Delta l'} &= k_1 - \text{const}\cdot\ln t.\end{aligned} \tag{17}$$

The use of Eqns. (13)–(17) makes it possible to calculate the rates of reactions Z + O_2 →inert product as a function of the degree of dispersion of the substance (metal, sulphide, etc.) and one can find the optimum conditions for the employment of the polymer stabilised by one or other active stabiliser.

If a highly active stabiliser Z exists in the polymer in an atomic, molecularly disperse, or finely disperse state, the rate of its oxidation is determined, as already stated, by the diffusion of oxygen into the specimen and the movement of the reaction front (in the absence of counter-current diffusion of Z) obeys a parabolic law rigorously.

IV. THE GENERATION OF HIGHLY ACTIVE STABILISERS IN POLYMERIC COMPOSITIONS

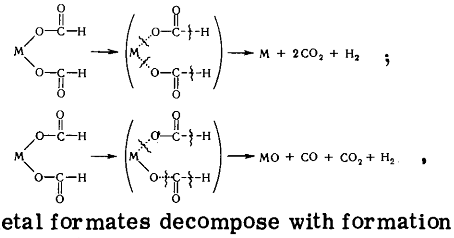
Many chemical processes yielding highly active compounds which are effective acceptors (absorbers) of oxygen or free radicals are known. Many of these reactions can be used for the high-temperature stabilisation of polymers or can serve as models for a detailed study of the mechanism of the inhibited ageing of thermostable polymeric materials. Naturally, in view of the wide variety of mechanisms of such processes, the conditions governing their occurrence, and the subsequent reactions of their products, in choosing the stabilising systems account must be taken of the characteristics of the particular polymeric system.

We shall consider a number of processes involving the generation of highly active stabilisers, which can serve as models. The formation of finely dispersed metals and lower-valence metal oxides from organic salts of the metals is of greatest interest[75,132,137].

Table 2. Temperature ranges corresponding to the decomposition of formates[156].

Formate	Temp. range of decompn., °C	Gaseous decomposition products
$Na(HCOO)$	320—420	H_2, CO, CO_2, CH_4 etc.
$K(HCOO)$	360—480	ditto
$Ca(HCOO)_2$	400—495	»
$Sr(HCOO)_2$	340—500	»
$Ba(HCOO)_2$	400—460	»
$Mg(HCOO)_2$	330—460	»
$Mn(HCOO)_2$	260—410	»
$Zn(HCOO)_2$	210—360	»
$Cd(HCOO)_2$	230—305	»
$Cu(HCOO)_2$	170—225	only H_2, CO, CO_2, and CH_4
$Co(HCOO)_2$	245—300	ditto
$Ni(HCOO)_2$	260—290	»
$Pb(HCOO)_2$	260—340	»

The decomposition of various formates, which can result in the formation of pyrophoric metals or their oxides is well known. Cobalt, nickel, copper, and lead formates decompose via the following mechanisms[156]:



while alkali metal formates decompose with formation of oxalates and carbonates:

$$2\,HCOOM \begin{cases} \nearrow M_2C_2O_4 + H_2 \\ \searrow M_2CO_3 + H_2 + CO \end{cases} .$$

Side reactions of the type

$$3H_2 + CO \rightarrow CH_4 + H_2O \quad ;$$
$$2H_2 + CO \rightarrow CH_3COH \quad ;$$
$$H_2 + CO \rightarrow HCHO \quad ;$$
$$2\,HCHO \rightarrow HCOOCH_3 \quad ,$$

occurring in the decomposition of these substances, lead to the formation of other products. However, the role of side reactions in the decomposition of cobalt, nickel, copper, and lead formates is small and the main products are M, MO, CO, CO_2, and H_2.

Tables 2 and 3 present data for the decomposition reactions of various formates[156].

Table 3. The ratios of the amounts of reaction products in the decomposition of certain formates[156].

Formate	$[M^{2+}]/[M^{2+}+M]$, %	$[CO]/[CO+CO_2]$, %	Formate	$[M^{2+}]/[M^{2+}+M]$, %	$[CO]/[CO+CO_2]$, %
$Co(HCOO)_2$	49.1	24.5	$Cu(HCOO)_2$	9.6	4.0
$Ni(HCOO)_2$	19.7	10.3	$Pb(HCOO)_2$	16.3	7.5

The metals and their oxides can be readily generated by the decomposition of the oxalates (Table 4). The process can be described by the general mechanism

$$M(COO)_x \rightarrow M + CO + CO_2 + M_nO_m \quad .$$

It presupposes the occurrence of various reactions of the following type[157-160]:

$$M(COO)_2 \rightarrow M + 2CO_2 \quad ;$$
$$M + CO_2 \rightarrow MO + CO \quad ;$$
$$M(COO)_2 \rightarrow MO + CO + CO_2 \; ;$$
$$MO + CO \rightarrow M + CO_2 \quad , \text{etc.}$$

The oxalates of transition metals, for example iron and nickel, decompose with formation by pyrophoric products:

$$FeC_2O_4 \rightarrow Fe + 2\,CO_2\,(FeO + CO + CO_2) \; ;$$
$$NiC_2O_4 \rightarrow Ni + 2\,CO_2,$$

while alkali and alkaline earth metal oxalates are converted into stable oxides on decomposition, for example:

$$MgC_2O_4 \rightarrow MgO + CO + CO_2 \quad .$$

Table 4. Temperature ranges corresponding to the decomposition of oxalates[159,160,162,163].

Oxalate	Temp. range of decompn., °C	Oxalate	Temp. range of decompn., °C
$Mg(COO)_2$	390—430	$Ni(COO)_2$	200—290
$Mn(COO)_2$	340—370	$Cu(COO)_2$	270—330
$Fe(COO)_2$	320—340	$Ag(COO)_2$	100—160
$Co(COO)_2$	310—330	$Zn(COO)_2$	310—350
$Ni(COO)_2$	260—320	$Pb(COO)_2$	310—370

The kinetics of the decomposition of oxides are frequently described satisfactorily by Erofeev's equation[157,159-161]:

$$\alpha = 1 - \exp(-kt^n).$$

When metals are used as radical acceptors, one must also take into account their efficiency as chain-transfer agents and their capacity to abstract certain atoms from molecules[181]. These reactions may lead to initiation rather than inhibition of the decomposition of the polymer.

At relatively high temperatures, polymer chain decomposition processes may be retarded by radical acceptors such as CO, SO_2, etc.; these compounds enter into copolymerisation type reactions, which lead to the formation of the radicals $R{-}CO^{\cdot}R{-}SO_2^{\cdot}$ and others which are less reactive than the initial radicals $R^{\cdot}$.[179]

The use of clathrate compounds occupies a special place among methods for the generation of stabilisers[4,182]. This procedure has been called the "structural-chemical stabilisation of the filler or stabilisers". A very active stabilising substance in such compounds is structurally isolated and cannot interact with oxygen and other chemical agents when it is introduced into the polymer. On the other hand, during heat treatment or employment of the polymer the clathrate compound decomposes with liberation of the stabiliser.

A satisfactory model whereby one can investigate the generation of a stabiliser of this type is provided by vinyl polymerisation in the presence of the amylose–I_2 complex[182]. The processes occurring in such a system can be represented as follows:

1. Decomposition of the initiator: initiator $\rightarrow 2R^{\cdot}_{pri}$ (w_{decomp}).
2. Decomposition of the clathrate compound (generation of the inhibitor): clathrate compound $\rightarrow I_2$ (w'_{decomp}).
3. Initiation: $R^{\cdot}_{pri} + Mo \rightarrow R^{\cdot}_i$.
4. Chain propagation: $R^{\cdot}_n + Mo \xrightarrow{k_p} R^{\cdot}_{n+1}$.
5. Biradical chain termination: $R^{\cdot}_n + R^{\cdot}_m \xrightarrow{k_0}$ products.
6. Chain termination by the inhibitor:

$$\begin{aligned} &R^{\cdot}_n + I_2 \xrightarrow{k'_0} RI + I^{\cdot} \quad ; \\ &R^{\cdot}_n + I^{\cdot} \xrightarrow{k''_0} RI \quad . \end{aligned} \tag{C}$$

Here $R^{\cdot}_{pri}$ is a primary radical, Mo the monomer, $R^{\cdot}$ the growing radicals, and w_{decomp} and w'_{decomp} are the rates of decomposition of the initiator and the clathrate compound.

It follows from mechanism (C) that the rate of inhibited polymerisation w_{inh} is

$$w_{inh} = k_p\,[R^{\cdot}]\,[Mo] = \frac{k_p}{k_0^{1/2}}\,[Mo]\,(w_{in} - w_{I\,gen})^{1/2} \quad ,$$

where w_{in} and w_{gen} are the rates of initiation and generation of the inhibitor. Next it is easy to show that the following relation holds:

$$\lg\,(w_n^2 - w_{inh}^2) = \text{const} - \frac{2E_p - E_0 + E_{gen}}{2.3\,R} \cdot \frac{1}{T} \, ,$$

where w_n is the rate of the non-inhibited reaction and the quantities E with the appropriate subscripts are the activation energies for the corresponding processes.

Fig. 1 presents the variation of $\lg w$ with $1/T$ for the case under consideration; evidently, at a certain temperature the process begins to be sharply retarded owing to the generation of a powerful inhibitor on decomposition of the clathrate compound.

V. INTERPRETATION OF CERTAIN QUANTITATIVE RESULTS

It is seen from the above data that there is much evidence for the mechanisms of both chain and non-chain inhibition of the ageing processes of thermostable polymers. The chain inhibition mechanisms have already been investigated for a long time, but many of these are based on all possible hypotheses and analogies: hardly any constants for the elementary processes are available. This is probably because of the lack of a single general mechanism of inhibited degradation. On the other hand, although the mechanisms of non-chain inhibition have been discovered only recently in many important instances[4], their validity can be readily demonstrated because of their considerable generality.

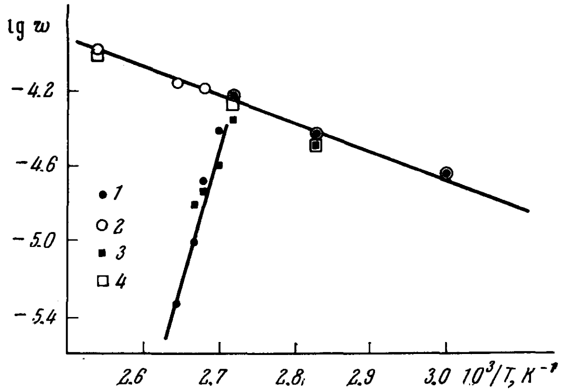


Figure 1. Variation of the logarithm of the rate of polymerisation of styrene at a constant rate of initiation with the reciprocal of temperature; $w_{in} = 3 \times 10^{-7}$ mole litre^{-1} s^{-1}; initiators: azobisisobutyronitrile ($T < 95°C$) and cumenyl peroxide ($T \geqslant 95°C$): 1) 18 g litre^{-1} of clathrate compound $\{[I_2] = 7 \times 10^{-4}$ M$\}$, dimethylformamide (DMF): styrene (ST) = 2.1; 2) clathrate compounds absent, DMF : ST = 2 : 1; 3) 18 g litre^{-1} of clathrate compound $\{[I_2] = 7 \times 10^{-4}$ M$\}$, DMF : ST = 5 : 1; 4) clathrate compounds absent, DMF : ST = 5 : 1.

Bearing in mind the possibility of non-chain inhibition in the presence of metal oxides, sulphides, and other compounds, it is possible to explain certain previously incomprehensible facts. Thus the stabilising activity of cobalt and other metal acetylacetonates[183] can be attributed not only to the termination of oxidation chains but also to the absorption of O_2 via a non-chain inhibition reaction. Similarly, other systems containing Co^{2+} [146,147,171] can convert oxygen into an ionic form and hence into a state which is inactive from the standpoint of the radical mechanism:

$$Co^{2+} + O_2 \rightarrow Co^{3+} + O_2^- \, . \tag{18}$$

It is noteworthy that reaction (18), which can be represented in the general case by Eqn. (3), is frequently one of the elementary stages in the chain mechanism and can also be classified as a non-chain inhibition process. However, the lack of quantitative data precludes the assessment of its importance in stabilisation.

The stabilising activity of certain sulphides[5], colloidal metals formed electrolytically in the polymer[75,184], and other compounds[53,67,72,185] can be attributed, as already pointed out, not only to a chain mechanism but also to a non-chain inhibition reaction between Z and O_2.

We have obtained a number of results which make it possible to demonstrate the possibility of the inhibition of the oxidative degradation of polymers by a non-chain procedure and to explain certain facts known previously. Thus the proposed stabilisation mechanism[4,37,113] operates when high-temperature oxidative ageing (300–500°C) of polyorganosiloxanes stabilised by active oxygen acceptors (Fe, Cu, Co, NiO, FeO, etc.), generated by the decomposition of the oxalates in the polymeric materials, is investigated. The non-chain mechanism of the stabilisation of polyorganosiloxanes in the presence of Fe, FeO, and Cu is proved by the following data:

1. The amount of oxygen acceptor generated in the polymer on decomposition of the oxalates corresponds to the amount calculated for the reactions

$$M(COO)_2 \rightarrow M + 2CO_2 \quad ;$$

$$M(COO)_2 \rightarrow MO + CO + CO_2 \quad .$$

2. As oxygen diffuses into the specimen, the entire metal (oxide) is converted into the corresponding stable oxide:

$$M + O_2 \rightarrow M_nO_m \quad ;$$

$$MO + O_2 \rightarrow M_nO_m \quad . \tag{19}$$

3. The polymer, which is almost immediately decomposed in the absence of a stabiliser, in the presence of metals (acceptors) begins to decompose vigorously only after the entire metal has been consumed.
4. The theoretical equation (12) holds satisfactorily.
5. The calculated value of τ agrees well with the experimental value.
6. The rates of reaction of O_2 with RH and $R^{\cdot}$, calculated from the rate constants and concentrations of the components, are much lower under the experimental conditions than the rate of reaction (19).
7. The stabilisation effect is determined by the ability of the metal or the lowest-valence metal oxide to form a stable oxide and by the rate of absorption of oxygen under the experimental conditions.

Data for the stabilisation of thermostable polymers in the presence of metals or their mixture with the lowest-valence metal oxides, generated on the decomposition of the oxalates and other compounds in polymers, are presented below. Henceforth it is assumed that oxygen is accepted by the metal–oxide mixture, which will be referred to for brevity as the metal.

Fig. 2 illustrates the variation of the relative elongation and tensile strength of a siloxane rubber. Evidently the specimens stabilised by finely dispersed metals retain their properties over a period 3–4 times longer than the specimens stablised by one of the best stabilisers known previously for this system—redoxide.

Table 8 shows that specimens of the polymer based on methylphenylsiloxane, stabilised by finely dispersed Fe and CoO, retain their properties within permissible limits for a longer period than the specimens stabilised by one of the best stabilisers based on a cerium(III) salt.

Table 9 presents data for the absorption of oxygen by specimens[112] containing finely dispersed metals generated in the polymer. Evidently the amount of absorbed oxygen is close to the value calculated for the reaction Z + O_2 → oxide; certain deviations from the calculated values are associated with the additional absorption of oxygen by the surface layer of polymer, after the consumption in the latter of the stabiliser, and with certain other unspecified factors.

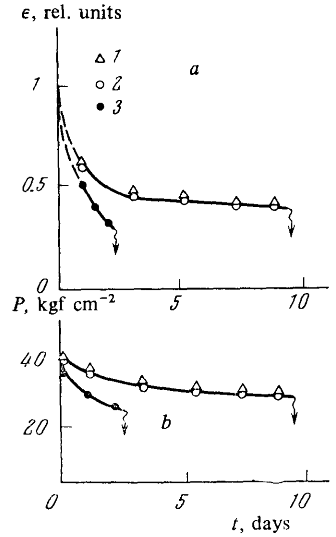


Figure 2. Variation of the relative elongation ϵ (*a*) and the tensile strength P (*b*) of methylphenylsiloxane rubber specimens during thermal ageing at 350°C: 1) stabilisation by finely dispersed Fe; 2) stabilisation by finely dispersed Cu; 3) stabilisation by Fe_2O_3 (redoxide); the arrows indicate the instant of decomposition of the specimens. The initial values of ϵ amount to 200–300%.

Table 8. The ageing of a polymer based on methylphenylsiloxane at 400°C in air [TiO_2 filler (30%); thickness of polymer specimen 1 mm (according to Shustova)].

Stabiliser (1%)	Time corresponding to retention of initial strength, h(P_0 = 15 kgf cm^{-2})	Time elapsed at instant corresponding to 60% relative elongation ϵ on rupture*, h
Without stabiliser	5.0	5.0*
Cerium(III) salt	7.0	10.0*
CoO	12.0	19.5*
Fe	24.5	19.5**

* ϵ_{init} = 100%.
** ϵ_{init} = 160%.

Fig. 3 illustrates the variation of the lifetime of trimethylcyclopolysiloxane films of different thickness in air at 400°C in the presence of finely dispersed iron[37] and Fig. 4 presents the kinetic curve for the absorption of oxygen. The region where the rate of absorption of O_2 represented by the curve in Fig. 4 decreases is consistent with the lifetime of the specimen τ_{crack} and corresponds to the instant of the complete consumption of the stabiliser via the reaction $Fe \xrightarrow{O_2} Fe_2O_3 + Fe_3O_4$. It also follows from

Fig. 4 that the initial rate of absorption of oxygen by the specimen w_{inh}^{i} is approximately four times greater than the rate of oxidation of the polymer w after the consumption of the stabiliser. Even if it is assumed that the oxidation of the stabiliser proceeds in the kinetic region, we have $4w = w_{\mathrm{inh}}^{i}$. The latter implies that the fundamental criterion of non-chain inhibition holds satisfactorily in the initial instant and the stabilisation under the given conditions is largely associated with the reaction of the finely dispersed iron with oxygen. Figs. 3 and 4 show that Eqn. (12) holds satisfactorily for the system investigated.

Table 9. The absorption of oxygen in the polymer by the stabiliser generated in a trimethylcyclopolysiloxane specimen (400°C).

Stabiliser	Reaction	Amount of O_2 absorbed by specimen, cm^3	
		calc.	expt.
Fe	$Fe + O_2 \rightarrow Fe_2O_3\ (Fe_3O_4)$	1.00	1.02
		1.28	1.33
Cu	$Cu + O_2 \rightarrow Cu_2O \rightarrow CuO$	1.00	1.05
		1.30	1.32

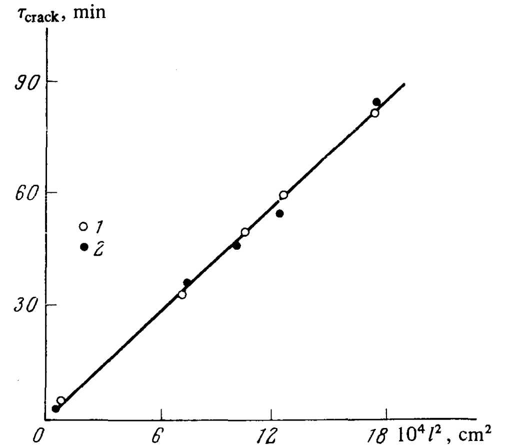


Figure 3. Variation of the lifetime τ_{crack} of hardened trimethylcyclopolysiloxane films stabilised by finely dispersed Fe {[Fe] = 0.3 mole kg^{-1}} with the square of the thickness of the specimen l^2 at 400°C; the lifetime of the specimens was determined from the cracking of the films (1) and from the absorption of oxygen (2).

Figs. 5 and 6 present the results[186,187] of the determination of the time required for the consumption of the stabiliser and the lifetime of polymer compositions based on trimethylcyclopolysiloxane stabilised by finely dispersed iron at 500°C. As the iron is converted into the iron(III) oxide, the intensity of the signal with $g = 2.0$ increases, the increase terminating at the instant τ_{ESR}.

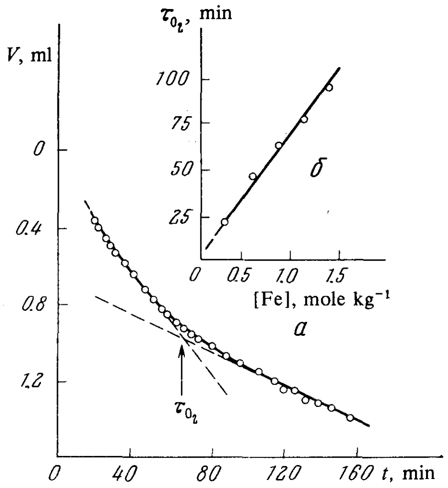


Figure 4. Kinetics of the absorption of oxygen by trimethylcyclopolysiloxane film {l = 140–150 μm, [Fe] = 0.3 mole kg^{-1}} stabilised by pyrophoric iron (a) and the variation of the lifetime of the specimen τ_{O_2} with the concentration of pyrophoric iron ($б$).

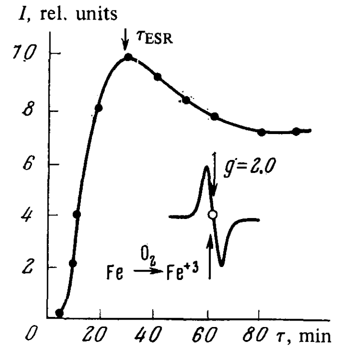


Figure 5. Determination of the time required for the consumption of the stabiliser τ_{ESR} in trimethylcyclopolysiloxane films {l = 160 μm, [Fe] = 0.3 mole kg^{-1}} by ESR from the variation of the signal intensity I (rel. units) at 500°C.

Thus the values of τ determined by the "cracking" method (τ_{crack}), by measuring the rate of absorption of oxygen (τ_{O_2}), and by ESR (τ_{ESR}) agree satisfactorily with one another[186,187].

It is noteworthy that, in the study of the degradation of thick films, deviations are observed from the parabolic law [Eqn. (12)], owing to the considerable absorption of oxygen by the polymer after the consumption of the stabiliser[39,110].

Table 10 lists the rates of the non-chain inhibition reaction $Z + O_2 \rightarrow$ oxide (recalculated in terms of the rate of the homogeneous process) evaluated to within a factor of 3 using the experimental data and the parabolic equation (13). It follows from Table 10 that the general phenomenological criterion (see Section III) $w_{Z+O_2} \gg w_{R+O_2}$, w_{RH+O_2}, w_{2RH+O_2} holds satisfactorily.

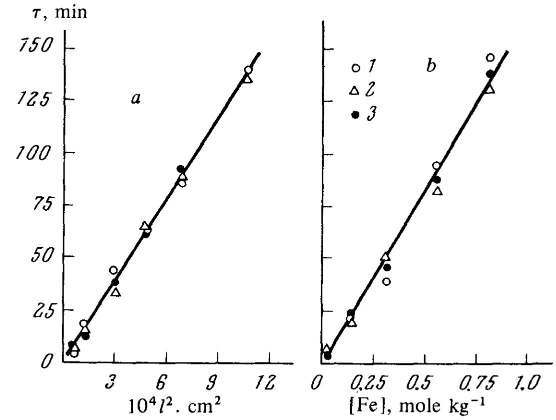


Figure 6. Dependence of the lifetime of trimethylcyclopolysiloxane polymeric films, stabilised by finely dispersed iron in the presence of components decomposing with evolution of H_2, on the square of the thickness of the specimen (*a*) and on the stabiliser concentration (*b*); the lifetime of the film specimens was determined from their cracking (1), from the absorption of oxygen (2), and by the ESR study of the consumption of the stabiliser (3).

Table 10. The rates *w* of the reaction between Z and O_2 in oxidative degradation calculated from experimental data[117,149,151,188] (350°C).

Stabiliser generated in polymer (5%)	Specific surface, $cm^2\ g^{-1}$	*w*, mole $litre^{-1}\ s^{-1}$
Fe	10	10^{-2}
	100	10^{-1}
Cu	10	10^{-1}
	100	1

The results presented suggest that, together with the chain inhibition methods, the procedures for the non-chain inhibition of oxidative degradation can be used successfully to stabilise many thermostable polymers.

Recently devised tests make it possible to estimate the reactivities of non-chain inhibition stabilisers[163]. Furthermore, a group of tests has been devised whereby one can estimate the reactivities of any inhibitors in radical chain reactions[40,189-191].

Apart from their practical importance, these studies are of theoretical interest. Thus it has been possible to show that the rate constants for many bimolecular radical reactions have a constant pre-exponential factor of $10^{7.2\pm0.2}$ (litre $mole^{-1}\ s^{-1}$) in the liquid phase and $10^{8.8\pm0.1}$ (litre $mole^{-1}\ s^{-1}$) in the gas phase[190,191]. Subsequently Tsepalov established that the pre-exponential factors for these reaction rate constants are different only in the case of radical substitution reactions. For many radical recombination reactions in both liquid and gaseous phases, the pre-exponential factors are $10^{8.8}$. It has also been established that the absolute values of the rate constants for these reactions in the gaseous and liquid phases are identical, which suggests that the rate constants are indeed elementary only for reactions with a constant pre-exponential factor of $10^{8.8}$ litre $mole^{-1}\ s^{-1}$. In reactions with a constant pre-exponential factor of $10^{7.2}$ litre $mole^{-1}\ s^{-1}$, the rate constants are apparently effective quantities produced by a combination of two or several elementary rate constants.

Studies have been published recently on the mechanism of the formation and degradation of metallopolymers[192-195]. It has been shown that these materials as well as certain polymeric and other heterogeneous compositions in which metals were generated[196,197] possess valuable properties. However, the increased resistance of these systems to thermo-oxidative degradation is not attributed by these workers[192-195], as in earlier studies[75,197], to the interaction of the active metals with oxygen, i.e. to non-chain inhibition processes[20,37,38]. As a rule, these studies[192-195,197] were carried out under conditions such that the rates of the thermal degradation reactions of the metallopolymers may be limited by the diffusion of oxygen and the degradation products. In many cases the high termo-oxidative stability of metallopolymers as well as polymers stabilised by metals[4,5,35,69,198] may be attributed not only to the nature of these materials but also to their stabilisation via a non-chain inhibition mechanism.

Interesting results have been obtained for the oxidation of polyethylene melts on metallic surfaces and in the presence of finely dispersed metals[199,200]; the characteristics of these processes can be explained in conjunction with known chain and non-chain inhibition mechanisms.

The non-chain inhibition of oxidative degradation at high temperatures is effective when pyrophoric lower-valence metal oxides, such as FeO and CoO, [37] sulphides, finely dispersed silicon, [201] and other oxygen acceptors[202,203] are used. The authors of this review have shown recently that the stabilisation of organosilicon coatings by FeO and by silicon makes it possible to increase by a factor of several tens their useful life at temperatures in the range 500–1000°C.

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Modern Ideas About the Mechanism of the Formation of the Structure of Graphitising Coke

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The review considers studies on the mechanism of low-temperature carbonisation, which determines the fundamental structural characteristics of carbonaceous materials. Particular attention has been devoted to the mesophase transformation as the principal factor responsible for the formation of the structure of graphitising coke. The structural features of various types of coke, whose formation proceeds via the mesophase transformation stage, are described.
The bibliography includes 53 references.

CONTENTS

I. INTRODUCTION

The unique properties of carbon-graphite materials have ensured their wide-scale application in various branches of modern engineering. The development of the technology of their manufacture has required the solution of many complex problems associated with the preparation of materials having specified properties. The principal raw materials in the technology of carbon-graphite materials are petroleum, pitch, and shale coke, which are converted into graphite on heat treatment at 2300°C and above. The raw materials for the preparation of such coke consist of heavy hydrocarbon residues from the processing of petroleum, coal, and bituminous shale.

It has been established by microscopy in polarised light that the above types of coke have complex and varied structures, but the mechanism of their formation remained unknown for a long time. The most realistic hypothesis [1] concerned the relation between the structure of coke and the complex chemical composition of the raw coking material, and the formation of particular regions in the microstructure was believed to be genetically linked to a particular group component of the raw material.

The ideas about the mechanism of structure formation in coke, which developed mainly on the basis of chemical research techniques, have been described most fully in the monographs of Krasyukov [1] and Onusaitis [2]. The inadequacy of these concepts became evident after Brooks and Taylor [3,4] and later a number of other workers [5,6] investigated by microscopy in polarised light the products of the low-temperature carbonisation of substances from which graphitising coke is obtained. Even before this, it was observed that the graphitising coke obtained at 450°C already had a textured layer structure [7,8]. It was also firmly established that graphitising coke may be obtained solely from substances melting at 350-500°C [9,10]; a characteristic feature of low-temperature types of coke, which makes it possible to infer unambiguously their capacity for graphitisation, is the presence of regions of optical anisotropy [11]. However, the most important stage in the understanding of the mechanism of structure formation in graphitising coke was the so called mesophase transformation discovered by Brooks and Taylor [3,4].

II. THE MESOPHASE TRANSFORMATION—THE MAIN STAGE IN THE FORMATION OF THE STRUCTURE OF COKE

1. General Description of the Phenomenon

The formation of the structures of all types of graphitising coke proceeds via the mesophase transformation. The latter occurs in the temperature range 390-520°C and consists of a phase transition in the liquid state during which large polymerised aromatic molecules in the isotropic mass of the pitch are arranged in parallel and form anisotropic liquid crystals of the mesophase [4]. The temperature range of the mesophase transformation varies somewhat for different substances and its extent depends significantly on many factors, which will be discussed below.

The liquid crystals of the mesophase arise in the isotropic liquid mass of the pitch, following an increase of temperature to 390-400°C, in the form of approximately 0.1 μm particles observed on ultrathin sections with the aid of an electron microscope, but Brooks and Taylor have no doubts about the existence at this stage of spherical formations of even smaller size. With increase of the temperature and the duration of treatment, the spherical formations grow in size and the proportions of the pitch and the mesophase change in favour of the latter. As long as the ratio of the phases in specified volumes does not exceed 1 : 1, the growth of the spherical formations takes place at the expense of the surrounding pitch; their shape remains rigorously spherical and their diameter may reach tens of micrometres. When the proportion of the mesophase is high, the coalescence of the individual spherical particles begins with formation of larger particles of different shapes (Fig. 1). At the instant of the complete conversion of the pitch into the mesophase, the multiple coalescence of the spherical particles results in the formation of a complex structure, which Brooks and Taylor [4] called the mosaic structure although it does not in fact consist of sharply delimited regions.

The structure of the mesophase spheres at the instant of their formation and during their initial growth was investigated by microscopy in polarised light[3,4,12], by electron diffraction[4], and by X-ray diffraction[13]. It was established that the mesophase spheres are optically monoaxial positive liquid crystals with straight extinction belonging to the hexagonal system. The planar aromatic layers are arranged at right angles to one diameter of the sphere becoming bent at its edges in such a way that they become perpendicular to its surface (Fig. 2). The distance between the layers is 3.43–3.49 Å. The fact that the planar molecules forming the sphere have a radial arrangement near the surface promotes the initial coalescence of the spheres. The coalescence results in the formation of mesophase regions with a more complex structure than that of the initial spheres.

Figure 1. Particles of the mesophase in coal tar pitch. Coalesced formations observed together with individual spheres. Polarised light; magnification × 350.

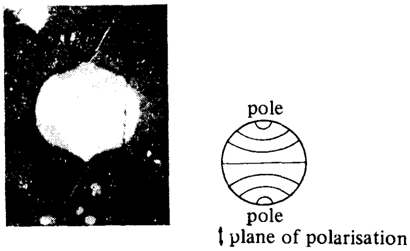


Figure 2. Sphere in which the lamellar layers are distributed at right angles to the surface of the polished section passing through the centre of the sphere. The "poles" refer to the ends of the principal axis of symmetry of the sphere. Polarised light[3].

At the instant of complete conversion of the pitch into the coalesced mesophase, the coking material consists of a very viscous liquid. At a somewhat higher temperature, the mesophase swells under the influence of the evolved gases and is converted into solid semicoke. During swelling, the mesophase is markedly deformed and the microstructure produced at this time hardly changes on subsequent heat treatment and on conversion into coke.

Different versions of the coalescence of the mesophase spheres and the resulting structures as well as the structures formed on deformation of the coalesced mesophase have been investigated in detail[12,14,15]. The relation between the microstructure of coke and the structure of the coalesced mesophase and its deformation has been described[16]. Owing to the high viscosity of the mesophase and the insufficient time during which it exists in the fused state, there is insufficient time during the coalescence of two and more spheres for the formation of a regular arrangement of their layers and a simple layer structure. Furthermore, the structural result of the coalescence depends on the mutual orientation of the C-axes of the coalescing spheres[12]. In the multiple coalescence of spheres, the above factors lead to the formation of a complex structure of the coalesced mesophase, including linear defects in the packing of the planar layers, discontinuities, and pronounced bending. The extensive deformation of the mesophase on swelling increases by several orders of magnitude the number of defect structures[12]. Linear defects are the preferred site of the generation of contraction cracks on subsequent heat treatment[15].

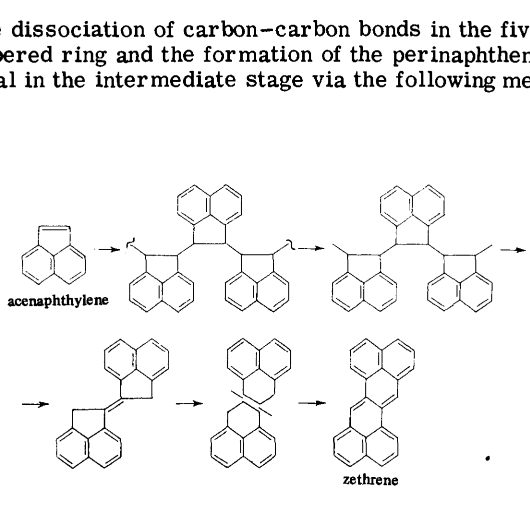
2. The Chemistry of Carbonisation Processes

The chemical composition of isotropic pitch in which the mesophase spheres are formed and grow is extremely complex. In broad outline, the chemistry of the processes occurring during coking in the temperature range 380 to 460°C is described as a sequence of thermal dehydropolycondensation reactions. Detailed studies on these processes involve considerable difficulties associated with the complexity of the chemical composition of the coking raw material and with secondary interactions—the recombination of radicals, mutual influence and interaction of various hydrocarbons with different activities, and polycondensation processes.

The mechanisms of coking reactions have been inferred[1,3] from the results of a detailed analysis of the volatile products and simple measurements of certain properties of the condensed phase, such as density, the C/H ratio, group composition, etc. In recent years vigorous research has been undertaken on the intermediate stages in the carbonisation process using ESR, ultraviolet and infrared spectroscopic, mass-spectrometric, and NMR methods. In combination with special methodological procedures, it was possible to obtain certain data on the mechanisms of the reactions occurring in the condensed phase.

Certain fundamentally important results were secured in the study of the carbonisation of individual hydrocarbons, including those forming graphitising coke, such as acenaphthylene, anthracene, phenanthrene, naphthacene, dibenzanthrene, etc.[17-20]. Acenaphthylene has been most thoroughly investigated. Its carbonisation was initially achieved via low-temperature polymerisation with subsequent thermal depolymerisation above 350°C, resulting in the formation of fragments which react, giving rise to larger condensed aromatic molecules[20]. The mesophase transformation in the carbonisation of acenaphthylene begins at 405°C.

Ruland[17] established by X-ray diffraction that the formation of carbon in the carbonisation of acenaphthylene proceeds via the formation of zethrene followed by condensation of the zethrene elements into extended polycyclic aromatic systems. This rearrangement is accompanied by the dissociation of carbon–carbon bonds in the five-membered ring and the formation of the perinaphthenyl radical in the intermediate stage via the following mechanism:



Singer and Lewis[18,19] studied the carbonisation of acenaphthylene and other aromatic hydrocarbons by ESR in order to identify the intermediate radicals generated and refine the mechanism of the chemical reactions occurring at various stages of the process. The ESR spectra of various types of semicoke usually observed consist of a single line without hyperfine structure, the width and intensity of which depend on the treatment temperature. Such spectra do not yield information about the free radical structures present in the carbonised system. In order to overcome this difficulty, the authors[17,18] carried out the carbonisation in an inert solvent—*m*-pentaphenyl. Dissolution decreased the probability of the combination of free radicals and thereby permitted their detection and identification by ESR. It was established[17] that the carbonisation of acenaphthylene proceeds via the scheme described by Ruland with the intermediate formation of the perinaphthenyl or dimethylperinaphthenyl radicals[17].

The results of the study of six different compounds led to the conclusion that the intermediates in the formation of large condensed molecules are free radicals arising as a result of the thermal dissociation of the bond at the most active site of the molecule. Depending on their reactivity, these aromatic free radicals can either condense with loss of hydrogen into large aromatic fragments or can undergo an internal rearrangement. If the intermediate free radical products have a planar configuration, then the carbonisation of the compound proceeds via the mesophase transformation and high-temperature treatment yields ordered graphite; on the other hand, when non-planar radicals are formed, the formation of the mesophase is not observed and the subsequent graphitisation is unsatisfactory.

Evans and Marsh[20] observed by mass-spectrometric measurements that the principal component of the carbonisation products at 405–500°C (the region of the mesophase transformation) is decacyclene, while at higher temperatures molecules with zethrene configuration begin to predominate. The molecules of both types are planar (in the decacyclene molecule the acenaphthylene units are inclined at an angle of 3° with respect to the plane) and their further condensation leads to the formation of large planar structures capable of an ordered arrangement to give the liquid crystals of the mesophase.

The mechanism of the carbonisation of anthracene, phenanthrene, and naphthacene is simpler and consists in the formation of dimers and trimers, which are capable, by virtue of their configuration, of giving rise to large planar structures, ensuring the formation of ordered graphite.

Extremely interesting results were obtained in a study of the products of the carbonisation of acenaphthylene at 625°C, i.e. after the completion of the mesophase transformation[20]. In order to investigate spectrometrically this high-molecular-weight involatile compound, it was subjected to hydrogenolysis by atomic hydrogen. The material treated in this way gave rise to a mass spectrum which contained peaks due to acenaphthylene, zethrene, decacyclene, acenaphthene, and zethrene dimers, whose intensities corresponded to their abundance. These results show that the carbonisation of acenaphthylene proceeds via identical condensation reactions over the entire region of the mesophase transformation.

The mass-spectrometric and elemental analytical data demonstrated only a slight difference between the compositions of the mesophase and the isotropic material from which it arises. On the basis of the results, the authors[20] concluded that the formation of the mesophase consists in the ordering of the molecules of the isotropic phase and not in the formation of other chemical structures.

In the coking of hydrocarbon raw materials of complex composition (pitches and resins) from which industrial coke is obtained, the chemistry of the processes is complicated by the factors mentioned above, but in the region of the mesophase transformation the fundamental nature of the chemical reactions and the physicochemical processes is the same as in the carbonisation of the individual hydrocarbons.

At the beginning of the mesophase transformation, the substances present in pitches largely consist of polynuclear hydrocarbons and certain nitrogen and oxygen compounds. The ^{1}H NMR spectrum of the soluble fractions from which the mesophase is formed shows that more than 90% of the protons are linked to aromatic rings[14,18]. The average molecular weight of these fractions is 390–450; a stronger absorption is observed in the ultraviolet spectrum in the range between 370 and 450 nm.

Under carbonisation conditions, these compounds decompose via a radical mechanism with evolution of an insignificant amount of hydrogen and subsequent formation of more complex coplanar regions.

The results of elemental analysis of the partly carbonised pitch ($C_{100}H_{53}O$) differ little from the results of the analysis of the insoluble mesophase residue ($C_{100}H_{49}O_{1.4}$), but their average molecular weights differ significantly, amounting respectively to 790 and 1700.[4,5]

Ihnatowicz et al.[5] believe that the insolubility of the mesophase and its higher density compared with the pitch (1.48 and 1.25 g cm^{-3} respectively) are a direct consequence of the fact that the mesophase consists of more highly polycondensed molecules.

Honda et al.[12] found by X-ray diffraction analysis and by measuring a number of physical properties of pitch specimens as a function of the carbonisation temperature and time that the activation energy for the processes occurring in the region of the mesophase transformation is 35–45 kcal mole^{-1}. According to the authors, the growth of the spherical particles of the mesophase is due to a rearrangement of the C–C bonds and the evaporisation of low-molecular-weight substances.

Magaril and coworkers[21,22] obtained similar results. They investigated by infrared spectroscopy, ESR, elemental analysis, and measurements of the molecular weights and densities the intermediates in the carbonisation of petroleum tars and asphaltenes at 350°, 390°, and 410°C in solution in transformer oil. The molecular weight of the asphaltenes (the benzene-soluble fraction), determined cryoscopically in naphthalene, was 940 and the molecular weights of carbenes (the fraction evolved from coke on extraction with carbon disulphide after the removal of benzene-soluble substances), determined osmometrically in carbon disulphide, were 135 600, 122 100, and 117 000 respectively at 360°, 390°, and 410°C. The authors concluded on the basis of ESR and infrared spectroscopic data that asphaltenes, carbenes, and carboids are substances of the same type. The fundamental difference between carbenes and asphaltenes is only a much higher (by two orders of magnitude) average molecular weight of carbenes and the difference between carboids and carbenes is insolubility of the former. The carboids may be insoluble, according to the authors, because their molecular weight is still higher than that of carbenes or because (and this appears much more likely) carboids are cross-linked three-dimensional polymers. It is noteworthy that the above study quotes molecular weights of substances soluble in carbon disulphide higher by almost two orders of magnitudes than the values given elsewhere[3-5,13].

The formation of coke in the thermal decomposition of asphaltenes is represented[22] as a chain process leading simultaneously to the formation of relatively low-molecular-weight products, carbenes, and carboids. The process activation energy obtained from experimental data is 58–60 kcal mole^{-1}, which corresponds to the dissociation energy of the weakest C–C bond in the asphaltene molecule.

The mesophase transformation usually takes place in the temperature range between 400° and 500°C. The conclusion that the same reactions take place over the entire temperature range was reached by Evans and Marsh[20] on the basis of mass-spectrometric data, by Ihnatowicz et al.[5], who demonstrated the constancy of the density of the mesophase and the pitch coexisting with the latter, by Huttinger[6] on the basis of the constancy of the H/C ratio for the mesophase, and by Magiril and Aksenova[22] on the basis of the constant yield of coke relative to the asphaltenes which have reacted and of the reaction rate constant.

Fialkov and coworkers[13,24] and Tyan[25] arrived at a similar conclusion. It has been established by ESR and microscopic methods that, in the range 400–450°C, i.e. from the instant of the generation of the spherolites until the complete conversion of the pitch into the mesophase, the concentration of the free radicals, the line width between the maxima of the derivative ESR absorption line, and the spin–lattice relaxation times remain unchanged, while below and above the limits of this range these characteristics change significantly. The authors concluded that the intramolecular structure of the mesophase responsible for the ESR signal does not change in the range 400–450°C and the formation of the mesophase is due to the increase of the size of the carbon network as a result of thermal degradation and the formation of new C–C bonds.

Thus it may be regarded as established, on the basis of comprehensive studies of the low-temperature carbonisation processes of individual hydrocarbons and their complex mixtures (pitches and tars), that the mesophase transformation involves the ordering of large planar aromatic molecules with formation of nematic liquid crystals accompanied by further condensation with slight losses of hydrogen. As a result of this, the mesophase becomes insoluble. The liquid crystal molecules are formed by reactions involving the thermal dissociation of bonds at the most active site in the molecules and condensation of the resulting free radicals to a large planar aromatic structure.

III. FACTORS INFLUENCING THE MESOPHASE TRANSFORMATION AND THE STRUCTURE OF COKE

The structure of coke is wholly determined by a process involving the generation, growth, and coalescence of the mesophase spheres and the subsequent deformation of the coalesced mesophase on swelling. The study of the factors influencing such processes and of their mechanism is therefore of enormous importance for the solution of the problem of the regulation of the growth of different types of coke.

1. The Coking Conditions

The principal factors influencing the generation and growth of the spheres are temperature and time[3-6,13,16]. There is a limiting temperature below which spheres are not generated even after very prolonged treatment. With increase of the duration of isothermal treatment, a large amount of the pitch is converted into the mesophase, but the time dependence of the increased conversion is asymptotic. At a higher temperature, much less time is needed for the attainment of the specified degree of conversion and the latter is determined solely by temperature. Honda et al.[13] showed that temperature and time are adequate process parameters in the range 390–430°C as regards their influence on the degree of conversion and the properties of the mesophase.

The temperature–time parameters can be used effectively to regulate the structure and properties of coke. Isothermal treatment in the temperature range of the mesophase transformation leads to the formation of coke with a more ordered structure[23]. At the same time there is a significant increase (by 5–8%) in the yield of coke[23,26]. The increase of the rate of coking does not affect the temperature of the onset of the formation of the mesophase, but significantly displaces towards higher temperatures the instant at which the transformation ends, extending thereby the temperature range of the transformation. According to Ihnatowicz et al.[5], a change in the rate of heating of coal pitch from 0.5 to 3 K min^{-1} increases the temperature at which the mesophase transformation is completed by 55 K. At a higher rate of carbonisation, smaller spheres and coke with a mosaic structure are formed. These structural changes are associated with the fact that, when the temperature range of the transformation is displaced towards higher temperatures, there is also an increase in the rate of formation of mesophase nuclei and there is insufficient time for the complete coalescence of the growing spheres.

2. The Composition of the Coking Raw Material

When the influence of the composition of the raw material on the structure of the coke obtained is examined, account must be taken of two aspects—the genetic relation between the structure formed and the composition of the raw material[1,27] and the mutual influence of the components during coking[1,20,28]. The role of the insoluble fractions present in the raw material will be discussed below. The hypothesis that definite components of the raw material are responsible for the formation of a particular type of coke structure[1,27] must be regarded as an exaggeration. The mutual influence of the components is most likely to affect the formation of the structure.

In mass-spectrometric studies of the carbonisation of mixtures of individual aromatic hydrocarbons, intermolecular reactions were not observed, but a decrease of the degree of pyrolysis of the individual components was noted[20]. According to the authors, the latter effect may be a result of the decrease in the intensity of the condensation reactions owing to the mutual dilution of the mixture by the components.

Levinter et al.[28] observed a decrease of the yield of coke in the simultaneous coking of asphaltenes and oils compared with the coking of asphaltenes alone. As a result of the mutual influence of the components, such a mixture behaves during coking as a single group component with intermediate properties. The capacity for graphitisation of the coke derived from asphaltenes alone is poorer than that of the coke obtained from the mixture. Levinter et al.[28] reached the conclusion (similar to that of Lewis and Singer[19]) that dilution of asphaltenes by oils decreases the rate of formation and growth of coke "crystallites", which favours an increase in the degree of order of the coke structure.

In a study of the kinetics of coke formation, Magaril[29] also concluded that there is a relation between the differences in the kinetics and the amounts of coke formed and the differences in the properties of the solvent used in the coking of asphaltenes. The addition to a poor solvent for asphaltenes of an effective solvent lowers the yield of coke, while in the decomposition of asphaltenes in an effective solvent coke formation begins only after the attainment of a threshold concentration. The authors explained their latter finding by the solvation of asphaltenes, preventing their condensation and the onset of coke formation.

The presence in the raw material of certain chemical elements, particularly oxygen, sulphur, and nitrogen, plays an important role in the coking process. In pitch, they usually form part of heterocyclic compounds. During pyrolysis, the presence of the above elements promote, on the one hand, dehydrocondensation accompanied by the formation of partly stable intermediate products and, on the other, the formation of cross links[30,31]. The appearance of such links at the early stages of aromatic condensation leads to the formation of rigid carbon with an extremely non-ordered structure. The formation of cross links and of a three-dimensional network at later stages gives rise to the formation of a highly condensed aromatic system. When the raw material contains halogen atoms (Cl, Br), the thermal stability of the compounds falls, since the energy of the C–Cl and C–Br bonds is smaller than that of the C–C and C–H bonds. Owing to their high affinity for hydrogen, fluorine and chlorine act like dehydrogenating agents[30].

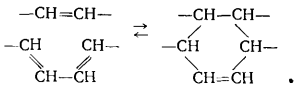
The influence of oxygen and sulphur on the mesophase transformation has been most thoroughly investigated. Ihnatowicz et al.[5] and also Tyan[25] established that the presence of more than 7% of oxygen in the raw material leads to the complete suppression of the mesophase transformation and to the formation of non-graphitising coke. When the oxygen content is less than 5%, the structure differs little from that of the usual graphitisable coke. Oxygen greatly narrows the temperature range of the mesophase transformation by reducing the temperature of its completion. When the oxygen content is 5–7%, coke with a pseudoisotropic structure is obtained. Sulphur has a similar influence on the mesophase transformation[31]. The presence of a small amount of sulphur does not cause appreciable changes in the properties of the mesophase, but, when its content exceeds a limiting concentration, for example 5% for PVC pitch, the fluidity of the mesophase and the temperature determining the limit of its plastic state decrease sharply. When the sulphur content is between 5 and 8%, fine spheres and a two-phase structure are formed. The presence of more than 8% of sulphur leads to the formation of an isotropic structure.

Kipling et al.[31] explain the effect of sulphur by the formation of cross links at the early stages of pyrolysis. They suggest the possibility of a catalytic effect of sulphur. It is postulated that the principal function of sulphur is to increase the degree of unsaturation of the molecules of the initial material:

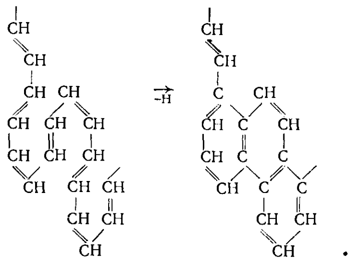
$$-CH_2-CH_2- + S \rightarrow -CH{=}CH- + H_2S \ .$$

The polyenes formed undergo Diels–Alder condensation reactions, which may be accompanied by dehydrogenation:

(a) intermolecular condensation:

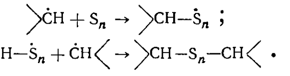


(b) intramolecular condensation:



At a fairly high temperature, one may expect that aromatisation will take place with elimination of hydrocarbons and hydrogen, which combines with sulphur to give hydrogen sulphide.

The reaction of sulphur with the free radicals produced in the pyrolytic process results in the incorporation of a certain amount of sulphur in the resulting structure:



$$\rangle\dot{C}H + S_n \rightarrow \rangle CH-\dot{S}_n \ ;$$
$$\rangle CH-\dot{S}_n + \dot{C}H\langle \rightarrow \rangle CH-S_n-CH\langle \ .$$

The radical formed, being comparatively long-lived, can react with other hydrocarbon radicals, forming cross links, which prevent the mutual orientation of the molecules.

It has been noted[15] that, despite the wide variety and complexity of the pyrolytic reactions, they can be characterised by the structure formed as a result of the coalescence of the mesophase spheres. Microstructure studies on different types of semicoke derived from starting materials with different contents of heteroatoms demonstrated a decrease in the size of the mesophase spheres with increase of the sulphur content. This finding can be accounted for by the increase viscosity of the mesophase due to the formation of cross links at early stages of the pyrolysis. The influence of increasing viscosity has also been noted by Kipling et al.[31]; the increase in viscosity complicates the reorientation of the molecules in the liquid stage.

3. The Influence of Additives

The influence of various additives on the coking processes has been investigated in many studies. All the additives employed can be divided, in terms of the nature of their activity, into chemically active, catalytic, and plasticising[32].

The most common way in which the properties of the coking raw material are affected is by oxidation with atmospheric oxygen or various chemical agents. When oxygen is passed through the starting material, peroxides are usually obtained in the first instance and are then converted into stable compounds on subsequent decomposition. The decomposition of peroxides may result in the formation of cross links leading to the formation of a rigid carbon structure[30]. The role of oxygen probably reduces to the initiation of the condensation and polymerisation reactions of multicomponent aromatic compounds present in the pitch owing to the formation of free radicals during oxidative dehydrogenation. The radicals can give rise to peroxide compounds, which initiate the subsequent process and also interact with one another, forming molecules capable of further growth[32].

Various substances are used to initiate the oxidation reactions. Variable-valence metal salts are familiar catalysts and the mechanism of their action has been investigated in detail[33-36]. The valence of the metal changes during the process and free radicals are formed, probably as a result of the direct involvement of the catalyst in the reaction between oxygen and the hydrocarbon. The role of the catalyst reduces to initiating the oxidation reaction in the initial stage of its development, which ensures as high a rate of chain initiation. However, Denisov[35] suggested the involvement of the catalyst also in the chain propagation processes, assuming that the catalysis takes place throughout the reaction via a sequence of macroscopic stages and not via a single mechanism. Peroxy- and azo-compounds are frequently used as initiators. Gas-phase initiation, where nitrogen dioxide produces the maximum effect, has been employed.

Apart from passing air through the starting material, many different oxidising additives are used; the influence of any of these can be accounted for by its effect on dehydrogenation and polycondensation processes. Sulphur is an agent closest to oxygen as regards its action. A mechanism has been put forward for its interaction[30]. When sulphur is added, the dehydrogenation temperature falls, and and, in addition, sulphurisation leads to aromatisation. The hydrogen liberated combines to form H_2S. Kipling et al.[31] made a detailed study of the mechanism of the catalytic action of sulphur present in the starting material. When sulphur is introduced at later stages of the pyrolysis, its role is to the dehydrogenation and aromatisation processes. In practice, when the pitch is treated jointly with sulphur and air, the carbonisation process is accelerated. The influence of aluminium chloride has been considered in a number of investigations[30,32,37]. Its catalytic action is probably based on the formation of intermediate complexes of the catalyst and the reactants.

Fitzer et al.[30], who investigated the influence of anhydrous $AlCl_3$ on the pyrolysis of different types of pitch, concluded that small amounts of the catalyst (0.1–0.5%) produce appreciable changes when the electron density in the aromatic ring is increased, for example by the presence of phenolic groups. Such compounds are always present in pitch. The favourable influence of the introduction of nitro-groups (NO_2) has been noted[38,39], the oxidative dehydrogenation of pitch being promoted. Such treatment of pitch is useful in connection with the reactivity of the nitro-group in dehydrogenation reactions and with its initiating effect on hydrocarbon oxidation processes[32].

The influence of boric acid and ammonium sulphate on the coking of petroleum residues has been examined[37]. It is suggested that these substances dissociate at 140° and 330°C respectively and promote the oxidative condensation of hydrocarbons of comparatively low molecular weights.

The influence of metals on coke formation in catalytic cracking is also noteworthy. Masagunov and Tikhanovskaya[40] concluded that the influence of the metal on coke formation depends on its dehydrogenating activity. Highly dehydrogenating metals (nickel, copper, and cobalt) lead to a sharp increase of coke formation even when their content is negligible.

Demidova[32] examined the influence of various types of additives, both chemically active (aluminium, bismuth, and potassium nitrates) and catalytic (finely dispersed nickel powder), directly on the mesophase transformation. The addition of aluminium, bismuth, and potassium nitrate increases the coking capacity as a result of condensation processes leading to the preferential growth of the content of carboids. The addition of finely dispersed nickel increases coke formation owing to the intensification of the dehydrogenation reactions of the low-molecular-weight compounds in the pitch in the range 200–300°C.

ESR and differential thermal analysis (DTA) data have shown that thermal degradation and the formation of the polymer structure of semicoke in modified types of pitch occur at lower temperature. Demidova[32] suggests that the formation of the semicoke structure in the modified pitch is completed at an earlier stage than in the initial pitch, as a result of the initiation of dehydropolycondensation processes mainly by the solid oxides derived from the decomposed metal nitrates. The introduction of condensing and catalytic dehydrogenating additives also promotes the initiation of the formation of mesophase spheres at 410°C. Mainly fine spheres are formed in the presence of additives. According to the author, the formation of the spheres and the limitation of their growth in pitch with added nitrates occur either in consequence of the shielding of their surface by the solid phase of the additive or because of the multiplicity of crystallisation centres, which may consist of finely dispersed oxides produced from the decomposed nitrates.

The decrease in the size of the spheres during oxidation was also noted by Averina[41], the increase in the number of spherical particles and the decrease of their dominant size being promoted by the increase of temperature and the rate of oxidation. An appreciable increase of the number of nuclei of the mesophase particles in the oxidised starting material was observed following the addition of catalysts, particularly iron(II) oxalate. According to the author, the catalyst prevents the coalescence of the mesophase particles, which leads to the formation of a fine-grained structure.

Oxygen and sulphur also increase the viscosity and the period of the mesophase transformation[15,31]. Kipling et al.[31] assume that the increase of viscosity, due to the increase of the degree of cross-linking of the molecules, complicates their reorientation and the formation of an ordered structure.

4. The Influence of Dispersed Additives; Mechanical and Other Influences

The influence of dispersed additives on crystallisation of high-molecular-weight compounds from the melt is generally known and is widely used to modify their structure. These additives are usually nucleus-forming agents and are present in the centres of the growing spherolites[42].

Brooks and Taylor[3] investigated the influence of various dispersed insoluble additives on the mesophase transformation and the structure of coke. They found that any solid surface constitutes the preferred site for the formation of the mesophase, but, in contrast to the crystallisation of polymers, dispersed additives remain on the surface and are never detected within the growing mesophase spheres (see Fig. 1). This factor significantly restricts the scope of the regulation of the structure and complicates the process. Because of this, the influence of dispersed particles on structure formation in carbonisation must be treated not only from the standpoint of the formation of nuclei but also taking into account their behaviour at the mesophase–pitch interface. Dispersed particles are almost always present in the starting materials from which coke is obtained. They differ significantly in structure and their behaviour in the coking process is likewise different[6,7,43,44].

Sedimentation of the dispersed components of pitch during its conversion into coke leads to large structural inhomogeneities along the height of the coke "pie"[6,44-46]. Numerous point structures, consisting of aggregates of the dispersed components of pitch, are observed in its lower part. The smallest particles remaining in the pitch at the instant of the onset of the mesophase transformation are distributed non-uniformly. After the appearance of the mesophase, they collect on the surface of the spheres and prevent their growth by depriving them of the ability to coalesce (Fig. 3).[16] The pitch phase is then liberated from the dispersed particles and the new spheres formed in it grow to a much greater size via coalescence. As a result, when the pitch is fully converted into the mesophase, the fine spheres blocked by the dispersed particles give rise to mosaic structures and the large spheres give rise to acicular, fibrous, streaming, or oriented structures (the differences between them are merely a matter of terminology).

The structure of coke obtained from starting materials containing dispersed particles is extremely inhomogeneous. In most cases where a readily graphitising coke is required with a homogeneous acicular or layer structure, one endeavours to liberate the fused pitch from the dispersed component with the aid of various technological procedures (filtration, centrifugation, etc.)[47,48]. It is also possible to obtain a homogeneous mosaic structure by introducing dispersed additives, which form a three-dimensional coagulation network throughout the bulk of the material and prevent the coalescence of the spheres[49].

Compact coagulation in the pitch phase, which is usually characteristic of the dispersed component of pyrolytic tars, leads to the formation of aggregates in the form of grains, whose size ranging from 0.5 to 5 mm upwards, known in the literature[43,46] as spherulitic structures. As a result of partial sedimentation, the content of spherulitic structures increases at the bottom of the coke "pie". When the viscosity of the pitch phase is fairly high, for example in the coking of the oxidised residues, the spherulites remain distributed throughout the bulk of the coke[44]. The dispersed components of the starting material, distributed in the main bulk of the coke, have the greatest influence on its properties. Thus insoluble dispersed particles play a very important role in the formation of the structure of coke and can be used to control it.

Apart from the factors described above, mention should be made of the effect of mechanical influences and the magnetic field on the structure of the mesophase. Simple stirring of the coke material at the stage of the mesophase transformation improves the coalescence of the spheres and rotary stirring, apart from intensifying coalescence, gives rise to a coaxial orientation of the aromatic layers in the coalesced mesophase and leads to the formation of textured coke[3,4].

The application of a 6.0 kG magnetic field for 1.5 h during the mesophase transformation causes the orientation of the *C*-axes of the spheres parallel to one another and to the direction of the magnetic field. Sanada et al.[50] suggest that such orientation of the spheres is caused by the forces arising from the effect of the magnetic field on the magnetically anisotropic polycondensed aromatic molecules in the spheres. These forces have been estimated approximately as 1–3 dyn g^{-1} from measurements of the magnetic susceptibility. The coalescence of the spheres results in an oriented mesophase, but defects are observed in the arrangement thus produced. According to the author, the forces generated by the magnetic field applied in the coalescence stage are too low to form a defect-free structure.

A specific type of mechanical influence on the coalesced mesophase of gaseous coking products plays a very important role in the formation of the coke structure. It is known[1,51] that the maximum rate of gas evolution in the coking process is observed at the temperature corresponding to the end of the mesophase transformation. Since the mesophase has a much higher viscosity than the pitch phase, it prevents free gas evolution and swells under the pressure of the gases evolved. During swelling, the volume of the coking mass increases by a factor of 4–9 [1] and its very rapid solidification, the mechanism of which has not so far been investigated, takes place. After swelling, the coalesced mesophase consists of a porous material with a spongy structure.

During the swelling process, the mesophase matrix is extended and deformed and its constituent layer structures are oriented in the direction in which the stretching stresses are applied. The mesophase is deformed most markedly at the sites which have become the walls between the pores and to a lesser extent at the functions of several walls. The layers of the mesophase are oriented along the walls, forming a texture within the limits of each. The instant at which swelling comes to an end and mesophase solidifies can be regarded from the morphological point of view as the instant of the termination of the formation of the coke structure. Intra- and inter-molecular rearrangement processes occurring on further increase of temperature do not have an appreciable influence on the structure.

Among the factors discussed above, influencing the mesophase transformation, the following have found the most extensive practical applications: regulation of the behaviour of the dispersed components of the starting material, isothermal treatment in the temperature range of the mesophase transformation, oxidation of the starting material at a temperature below the onset of the mesophase transformation. The first two factors are usually employed to obtain anisotropic types of coke with a distinct oriented layer structure, which are readily converted into graphite and have a high electrical conductivity and reactivity. For this purpose, the coking starting material is freed from solid particles at a temperature below the onset of the mesophase transformation by filtration, centrifugation, or by being allowed to stand[47,48]. Oxidation of the starting material is used to obtain coke with isotropic properties[41].

IV. STRUCTURAL CHARACTERISTICS OF VARIOUS TYPES OF COKE

The structures of all types of graphitising coke are based on layer structural elements formed in the stages of the mesophase transformation and on subsequent deformation during the swelling of the mesophase. In this sense, the structure of each type of coke can be fully described by the dimensions and nature of the relative disposition of these structural elements[41]. Furthermore, different industrial types of coke have structural features, which are wholly determined by the composition and properties of the starting material from which they are obtained, mainly by its content of insoluble substances, its reactivity, and the degree of its oxidation[1,16,41,43,45,46].

There is as yet no established terminology in the literature for the structure of coke. This is because studies on the structure of coke have been carried out for a long time without understanding the mechanism of its formation. For this reason, the apparent wide variety of structures could not be treated systematically and each investigator, concentrating attention on a particular aspect of the same layer structure, characterised it by a specific terminology based mainly on morphological considerations. Thus terms such as acicular[47,48], fibrous[45,52], and streaming[41,43] structures arose to characterise sections of the mesophase structure with layers oriented in the direction of stretching on swelling. Much attention has been given to problems of terminology in a study by Averina[41]. Some of the morphological terms and the associated errors have been criticised[16,46], but this problem is outside the scope of the present review.

The following concepts can be used to characterise the structure of coke. The structure of coke is understood as the collection of all the structural elements and their combinations which are encountered within coke. The structure can be simple or complex depending on whether it consists of one or several types of structural elements; it can be homogeneous or inhomogeneous depending on whether the elements are of equal size and have the same orientation and on whether or not their distribution in the bulk phase is uniform. When structural elements of a single type form accumulations in a complex structure in the form of grains or other aggregates, then regions with a structure of the same type are usually referred to as structural components. Finally, a structural element is understood as a morphological unit with optically definable boundaries, characterised by a particular shape and internal structure.

The formation of coke with a specified structure and properties by active interference with the coke formation process has not yet been developed widely on an industrial scale and this is why industry produces a limited range of types of coke, the structure and properties of which are wholely determined by the type of raw material used in the coking process. The starting materials for the preparation of graphitising coke are the heavy residues from petroleum processing and the products of the processing of the tars resulting from the coking of coal and bituminous shale[1,41,51]. The temperature conditions in the prepration of the coking raw material have a definite influence on the structure of coke. Accordingly, all kinds of raw material can be divided into three types[41]: low-temperature raw material—the cracking residue obtained at 500–600°C and virtually free from solid particles; moderate-temperature raw material—the pyrolysis tars obtained at 650–800°C and containing different amounts of 0.5–4 μm solid spherical particles with a radial ray internal structure; high-temperature raw material— coking tars obtained at 800°C and above and containing solid soot particles smaller than 0.1 μm. The insoluble dispersed components of the raw material are the basic cause of the formation of the complex and inhomogeneous structure of coke[16,41-46]. Certain characteristics of the different types of raw material, based on the data published by Krasyukov[1] and Stepanenko et al.[51], are presented in Table 1.

Table 1. Characteristics of different types of coking raw material.

Parameter	Cracking residue	Pyrolytic tars mild regime	Pyrolytic tars severe regime	Coal tar pitch
Density, g cm^{-3}	0,94	1,12	1.17	1.33
"Ring and sphere" softening temperature, °C	liquid	liquid	liquid	145
Group composition, wt.%	74	82	66.5	28
Tar malthenes	21	9.8	8.7	
Asphaltenes	5	7.1	12.3	24
Carboids	0.3	1.0	12.5	48
Sulphur content, %	0.4	0.5	0.5	0.7
Coking number, %	9.0	18.1	30.4	74.0

The temperature of the processes in which the coking raw material is obtained determines not only its content of dispersed components and their structure[41,44] but also its reactivity and a number of other properties[1] influencing its behaviour in coking and the structure of the coke obtained.

We shall now consider the structural characteristics of the commonest industrial types of coke. The petroleum-cracking electrode coke (PCEC) is obtained by the coking in stills of a low-temperature raw material–the petroleum cracking residues[1]. This coke has the simplest and most, homogeneous structure among all industrial types of coke, consisting only of lamellar structural elements, forming sections of a structure with a parallel orientation in the walls between the pores and sections with a randomly oriented structure at the junctions of several walls (Fig. 3). The formation of a simple structure is ensured by the absence from the coking material of dispersed components and the only structural inhomogeneity is the orientation inhomogeneity, unavoidable in coking within the bulk of any raw material and associated with the inhomogeneous deformation of the coalesced mesophase on swelling.

Petroleum pyrolytic coke is obtained by the coking in stills of a moderate-temperature raw material—pyrolytic tars[1]. Depending on the pyrolysis temperature, tars corresponding to mild (650–700°C) and severe (750 to 800°C) regimes are distinguished. The mild regime tar is distinguished by a much higher content of carboids. The carboids in pyrolytic tars consist of solid spherical particles with a specific radial ray structure (Fig. 4), which are converted into the coke structure without a change in morphology[43]. For this reason, a characteristic feature of all pyrolytic types of coke is a layer structure consisting of two types of structural elements—spherical elements with a radial ray internal structure and lamellar elements forming the base of the coke. The behaviour of the spherical particles in the coking of mild or severe regime pyrolytic tars is significantly different; this determines also the difference between the structures and properties of the corresponding types of coke.

Figure 3. Petroleum cracking electrode coke. Randomly oriented structure. Replica; magnification × 3500.

Figure 4. Spherulitic structural component of petroleum pyrolytic electrode coke. Replica; magnification × 7000.

The petroleum pyrolytic electrode coke (PPEC) is obtained from mild regime tars. In the coking of such tars, the spherulites coagulate with formation of dense aggregates in the form of grains whose size ranges from a fraction of a millimeter to 4–5 mm [43,46]. Such aggregation takes place until the onset of the mesophase transformation and for this reason the spherulites of the starting material do not have a significant influence on the growth of the mesophase spheres. As a result of aggregation, the spherulitic structural elements form the spherulitic structural component of the PPEC, which is usually located at the base of the coke or in the form of grains at the junctions of several interpore walls. The base of the coke, made up of the mesophase deformed on swelling, consists mainly of a larger structure with parallel orientation. Thus the PPEC structure can be characterised as complex and inhomogeneous, having spherulitic and lamellar structural components with parallel orientation (Fig. 5).

The special petroleum pyrolytic coke (SPPC) is obtained from severe regime tars. Despite the much higher content of sperulites in such tars, they do not coagulate on coking. Remaining uniformly distributed in the coking raw material, the dispersed spherulites prevent the growth and coalescence of the mesophase spheres. This factor and also the packing defects introduced by the spherulites into the structure on deformation of the mesophase matrix during the swelling process rule out the possibility of the formation of structures with parallel orientation. Because of this, SPPC has a complex relatively homogeneous structure consisting of a matrix comprising lamellar randomly oriented structural elements and filled by spherulitic structural elements. Such a structure is referred to[41] as impregnated-spherulitic. The spherical structural elements are sometimes encountered in the form of aggregates, but the latter do not form a clear-cut boundary with the rest of the matrix. The causes of the different types of behaviour of spherulites during the coking of mild and severe regime tars have not as yet been elucidated. It is suggested[41] that the absence of coagulation is associated with the lower reactivity and greater viscosity of the severe regime tars.

Figure 5. Petroleum pyrolytic electrode coke; magnification × 49.

The pitch electrode coke (PEC) is obtained from a high-temperature raw material—coal tar pitch. The starting material consists of coal tar pitch— a side product from the coking of coal containing, apart from various hydrocarbons, a fairly large amount of soot particles, formed in the coking furnace from gaseous coking products in the concluding stage of the process at temperatures of 900°C and above, and also very small solid particles consisting of certain components of coal. Coal tar is converted into pitch by oxidation, usually carried out by blowing hot air through the tar at 250–300°C. The purpose of the oxidation is further condensation and increase of the yield of coke. PEC has a complex inhomogeneous structure, the formation of which is determined mainly by the behaviour of the soot particles of the raw material in the mesophase transformation stage[16]. The partial sedimentation and aggregation of the largest particles lead to the formation of the so called point structural components (Fig. 6). The smallest of these also remain distributed in the pitch at the instant of the formation of the two liquid phases evolved from it on the surface of the growing mesophase spheres, blocking their growth and preventing their mutual orientation and coalescence. The distributed particles significantly increase the proportion of defects in the lamellar structural component of the pitch coke (Fig. 7).

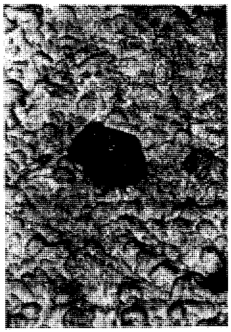


Figure 6. The point structural component of pitch electrode coke. Replica; magnification × 7000.

Figure 7. Pitch electrode coke; magnification × 350.

Different types of shale coke, obtained from the heavy residues remaining after the processing of bituminous shale, have been used increasingly in recent years in the manufacture of carbon-graphite materials. Depending on the purpose of the processing (the formation of petrol, gaseous hydrocarbons, etc.) and its temperature, the residues obtained differ significantly in composition and properties, which determines the wide variety of structures and properties of shale coke[43]. Thus the shale coke from the pyrolytic tars of shale petrol has a structure analogous to that of PPEC, while the structure of the coke from the "gas" tar is analogous to that of PCEC.

Table 2 presents some of the properties of industrial types of coke in accordance with the USSR Government Standards GOST 3278-62 and GOST 3213-58 as well as other data[1,41,45]. Ultimately, almost all the properties of coke are determined by the degree of development of structural anisotropy, arising at the mesophase transformation stage, and by the structural characteristics associated with the dispersed components of the coking raw material. In terms of increasing anisotropy, the types of coke described above can be arranged in the following sequence[41]: PEC < SPPC < PPEC < PCEC. The density of coke is associated directly with the structural anisotropy: the smaller the degree of development of anisotropy the lower the density (Table 2).

Table 2. Characteristics of certain types of coke.

Parameter		PCEC	Streaming component	Spherulitic component	SPPC	PEC
Pyknometric density, g cm^{-3}	1300°	2.10	2.08	2.02	2.04—2.08	2.085
	2400°	—	2.26	2.20	2.19	2.23
Graphitisability d_{002}, Å		3.364	3.369	3.385	3.388	3.380
Degree of graphitisation, %		—	54.5	36.5	70	—
Porosity, % (1300°C)		67—69	64—65		—	55—57
Press characteristics						
Relaxation coefficient, %		—	5.2	8.1	15.2	—
Coefficient of elastic expansion, %		10.4	14	6.7	8.4	7.3
Microhardness, kgf mm^{-2}	1300°	115	124	195	180	180
	2400°	7.2	10.5	30,2	21.5	13.6
Susceptibility to wear, %		6.0	10.5		6.4	8.0
Compressive strength	1300°	—	48		65	—
	2400°	—	16—44		38—43	—
Reactivity						
Oxidation in air	crude	97.0	92	—	—	—
	1300°	17.0	2.0	—	—	—
	2400°	0.10	0.17	0.32	—	—
Reduction in a stream of CO_2	crude	77.8	9.7		—	16.9
	1300°	17.0	7.5		—	6.0
	2400°	4.8	4.9		—	—

The decrease of the anisotropy of coke is a result of the comminution of the mesophase spheres during coking or of the oxidation of the coking raw material (PEC) or it occurs under the influence of the dispersed components (PEC, SPPC, PPEC). The latter cause the greatest decrease of density when they remain distributed within the bulk of the coke, as, for example, in PEC and SPPC. In this case, the decrease of the density of coke is associated not only with packing defects at the boundaries of the former mesophase spheres but also with the structural defects, which arise at the boundaries between the dispersed particles and the mesophase at the instant of the deformation of the latter on swelling. These defects consist of wedge-shaped pores, apparently mostly closed pores, since they arise as a result of the breakdown of continuity in the microvolume on deformation and not as a result of gas evolution; the pore size depends on the size of the dispersed inclusions. For example, the density of SPPC with 0.5–4.0 μm dispersed particles is significantly lower than the density of PEC with dispersed particles whose size is less than 0.1 μm.

Structural anisotropy is closely related to the capacity of coke for graphitisation (their capacity for conversion into graphite at temperatures above 2300°C), which determines in its turn very many properties, for example electrical conductivity, strength, reactivity, and antifriction properties. The conditions necessary for a satisfactory graphitisability, first formulated by Franklin[53], involve a mutually parallel orientation of crystallites and the absence of cross links between the aromatic layers at the edges of the crystallites.

The oxidation of the coking raw material at a temperature below the range of the mesophase transformation has the strongest influence on the graphitisability of coke. Oxidation immediately impairs both conditions for satisfactory graphitisability, since, together with the comminution of the mesophase spheres and the sharp decrease of anisotropy, cross links are formed in the oxidation process between the aromatic layers in the form of oxygen bridges. The dispersed components of the raw material affect only the first condition for graphitisability.

Among the types of coke described above, PEC graphitises least satisfactorily, since it is obtained from the types of pitch described above which contain a large amount of dispersed components, while PCEC graphitises most satisfactorily.

Structural anisotropy and the properties associated with it determine to a large extent the technological behaviour of coke and the properties of the articles made from it.

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The advances in recent years in the understanding of the mechanism of structure formation of graphitising coke have served as a basis for the development of new methods for the preparation of coke with a specified structure and properties. The development of a new class of one-component carbon-graphite materials, the so called "mesophase carbons" with a regulated structure and properties, is being prosecuted at the present time on the basis of the above advances. At the same time, vigorous research is being continued on the structure and properties of mesophase products of different origins and also on the synthesis of new substances, the heat treatment of which results in the formation of a mesophase with the required properties and capable of being converted into carbon on subsequent carbonisation without a significant change in structure. Further study of the mechanism of the mesophase transformation and of the formation of the structure of graphitising coke is one of the fundamental trends in the chemical technology of carbon and the science of carbon-graphite materials.

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Investigation of the Formation of Complexes of Organic Molecules and Lanthanide Ions in Solutions by the Electronic Energy Transfer Method

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Studies on the non-radiative energy transfer between organic molecules and lanthanide ions in solutions and on the utilisation of this phenomenon in the investigation of coordination-chemical processes involving lanthanide ions are reviewed.
The bibliography includes 98 references.

CONTENTS

I. INTRODUCTION

We considered previously[1] the non-radiative energy transfer between organic molecules and transition metal (TM) ions and its application in the study of the mechanisms of photochemical reactions of coordination compounds. The description of the experimental data in the review was preceded by a brief account of modern ideas about the mechanisms and kinetics of non-radiative energy transfer processes[†].

This review is devoted to studies of energy transfer between organic molecules and lanthanide ions in solutions. The mechanisms of energy transfer involving transition metal and lanthanide (Ln^{3+}) ions have much in common, but there are also differences. One of these is due to the fact that the chromium(III) and cobalt(III) coordination compounds, which have been most thoroughly investigated from the standpoint of energy transfer and photochemistry, exchange ligands with the surrounding medium very slowly[2]. In the case of lanthanide ions, the exchange with the solvent is fairly rapid, so that the luminescence processes and the processes involving energy transfer from and to lanthanide ions show behaviour averaged over the lifetime of their excited state. Another difference is the relatively low sensitivity of the positions and intensities of the bands in the absorption and luminescence spectra of lanthanide ions to changes in the environment compared with transition metal ions. The latter factor facilitates the study of the mechanisms of energy transfer involving lanthanide ions. For this and other reasons, the mechanism of energy transfer with participation of lanthanide ions has now been elucidated more effectively than the mechanism of the same processes involving transition metal ions. All these factors made it possible to use the energy transfer phenomenon to study complex formation reactions between lanthanide ions and organic molecules in the ground and excited states. The application of these methods has already made it possible to observe a number of new phenomena, for example the formation of hitherto unknown types of ion pairs by lanthanide ions and anionic dyes and of stable complexes between aromatic ketones and lanthanide ions, permitted an estimate of the rate of insertion of a ketone in the solvation shell of an excited lanthanide ion, etc. The prospects resulting from the application of the energy transfer method in the study of coordination-chemical processes are discussed below. These methods will probably find wide-scale applications in chemical research by virtue of their simplicity and wide scope.

II. INDUCTIVE-RESONANCE ENERGY TRANSFER BETWEEN ORGANIC MOLECULES AND LANTHANIDE IONS IN SOLUTION

1. Energy and Electron Transfer from Organic Molecules in the Fluorescent State to Lanthanide Ions

For a long time, it was widely believed[3-5], on the basis of several experiments which yielded negative results, that the fluorescence of organic compounds is not quenched by lanthanide ions. Thus Rollefson and Stoughton[6] in 1941 did not observe significant quenching of the fluorescence of quinine sulphate, fluorescein (cation), anthracenesulphonic acid, and acridonesulphonic acid by La^{3+}, Er^{3+}, Sm^{3+}, Pr^{3+}, and Nd^{3+} ions in water. Later Weiss[7,8] and Linshitz and Pekkarinen[9] were likewise unable to observe such quenching for several organic compounds.

Ermolaev and Shakhverdov[10] observed that the fluorescence of a number of dyes and aromatic hydrocarbons in solutions is strongly quenched by lanthanide ions when their fluorescence spectra overlap the most intense absorption bands of the ions. The narrowness of the absorption bands of the lanthanide ions made it possible to avoid the filtering and reabsorption effects in the quenching of the fluorescence. The dependence of the extent of quenching of the fluorescence q_0/q and of the decrease of the fluorescence lifetime (τ_{fl}) on the lanthanide concentration was found to be linear. The proportionality of the quenching rate constant to the overlap integral of the spectra ($\int_0$) shows that the fundamental quenching mechanism involves the inductive-resonance dipole–dipole (*dd*) energy transfer (Table 1) via reaction 1[‡]. The energy level diagram for the above type of transfer, i.e.

$$ {}^1D^* + Ln^{3+} \rightarrow {}^1D + (Ln^{3+})^*, \qquad (1)$$

[†] The fundamental definitions and the significance of the quantities used in the present review were also given in the previous article[1].

[‡] Here and henceforth D, A, Ln^{3+} on the one hand and D^*, A^*, and $(Ln^{3+})^*$ on the other denote the energy donor molecule, the energy acceptor molecule, and the lanthanide ion in the ground and lowest excited states respectively.

is illustrated in Fig. 1. The hypothesis of energy transfer in such systems was confirmed by the observation of the luminescence of Nd^{3+} in the 8 : 1 $POCl_3$–$SnCl_4$ system sensitised by organic compounds (rubrene, trypaflavine, Acridine Orange, Acridine Yellow, etc.). The experiments on the flash photoexcitation of the systems also showed that the quenching of the fluorescence of organic compounds is not associated with their induced transition to a triplet state in the presence of paramagnetic heavy metal ions[10].

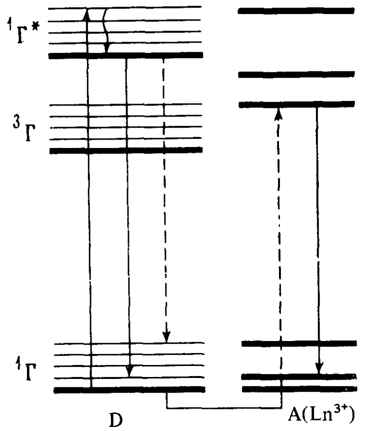

Figure 1. Schematic representation of the electronic levels in the energy transfer from organic molecules in the fluorescent state ($^1\Gamma^*$) to lanthanide ions.

The quenching of fluorescence by the Eu^{3+} ion, for which the $k_q/\int_0$ ratio is anomalously high (Table 1), involves reversible electron phototransfer via the mechanism

$$^1D^* + Eu^{3+}(^7F_0) \rightarrow {}^2D^+ + Eu^{2+}, \qquad (2)$$

as shown by Shakhverdov[11]. The Eu^{3+} ion exhibits the highest electron affinity among all the tervalent lanthanide ions[12] and can be readily reduced to Eu^{2+}. The constant k_q depends mainly on the ionisation potential of the organic molecules in the excited singlet state $I_p - E_{exc}$ (Table 2). In the flash photoexcitation of aromatic hydrocarbons in various solvents (acetone, methanol, etc.) in the presence of Eu^{3+}, a short-lived absorption due to their radical-cation ($^2D^+$) was observed; this decayed according to second-order kinetics[11]. The temperature variation of the quenching of the fluorescence of organic compounds by Nd^{3+} and Eu^{3+} ions also indicates different mechanisms of quenching by these ions.

Eisinger and Lamola[13,14] likewise found that the fluorescence of a number of biologically important compounds (for example tryptophan) is quenched by Eu^{3+} ions in H_2O and D_2O. They attributed this to energy transfer via molecular collisions, since the constant $k_q = 5 \times 10^9$ litre × mole^{-1}s^{-1} for tryptophan proved to be close to the rate constant for the reaction controlled by diffusion ($k_d \simeq 7 \times 10^9$ litre mole^{-1} s^{-1}). On this basis, they suggested[15] that Eu^{3+} be used to determine the decay times of the fluorescence of other compounds (nucleotides), assuming that $k_q = k_d$ in this case too. However, the absence of the sensitised luminescence of Eu^{3+} in the quenching of the fluorescence of tryptophan provides no grounds for such conclusion. The quenching of the fluorescence of tryptophan by the Eu^{3+} ion is probably due to reversible electron phototransfer via mechanism (2). Recent experiments by Ricci and Kilishowski[16] on the quenching of the fluorescence of indole derivatives by lanthanide ions confirm this view. They found that the Eu^{3+}, Yb^{3+}, and Sm^{3+} ions, i.e. those showing the greatest tendency towards reduction to the bivalent state, exhibit the strongest quenching effect, the rate constants for quenching by Yb^{3+} and Sm^{3+} ions being appreciably lower than the rate constant for diffusion through the solvent.

Table 1. The quenching of the fluorescence of organic compounds by lanthanide ions in acetone (293 K, in air)[10].

Donor	Acceptor	$10^{-9}k_q^*$, litre mole^{-1} s^{-1}	$10^{18}\cdot\int_0^{**}$	$10^{-26}\cdot k_q/\int_0$
Acridine Yellow	Nd^{3+}	11	7.4	14.9
	Er^{3+}	4.2	5.3	7.9
	Pr^{3+}	1.8	1.8	10.0
	Sm^{3+}	<0.1	0.9	—
	Eu^{3+}, Gd^{3+}, Ce^{3+}	<0.1	0.0	—
Perylene	Eu^{3+}	6.4	0.02	3200
	Ho^{3+}	4.3	9.6	4.5
	Pr^{3+}	2.2	6.6	3.3
	Nd^{3+}	1.7	1.6	10.6
	Ce^{3+}	0.1	0.0	—
Anthracene	Eu^{3+}	7.7	0.52	148
	Er^{3+}	1.5	1.6	9.4
	Pr^{3+}	1.0	1.1	9.1
	Dy^{3+}	0.5	0.6	8.3
	Sm^{3+}	0.4	0.6	6.7
	Nd^{3+}	~0.1	0.3	—
	Ce^{3+}	<0.1	0.0	—

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* k_q is the rate constant for the quenching of the fluorescence of organic compounds by lanthanide ions.

** $\int_0 = \int_0^\infty I_D^H(\nu)\epsilon_A(\nu)\nu^{-4}d\nu$ is the overlap integral of the spectra; $I_D^H(\nu)$ is the distribution of the quantised spectral density, normalised with respect to a unit area, in the fluorescence spectrum of the energy donor and $\epsilon_A(\nu)$ is the decadic molar extinction coefficient of the energy acceptor. The values of ln 10 $\int_0$ were adopted as the "overlap integrals" in the study of Ermolaev and Shakhverdov[10].

Table 2. The quenching of the fluorescence of organic compounds by Eu^{3+} (acetone, 293 K, in air)[11].

Electron donor	$I_p - E_{exc}$, eV	k_q, litre mole^{-1} s^{-1}	Electron donor	$I_p - E_{exc}$, eV	k_q, litre mole^{-1} s^{-1}
Anthracene	4.05	$7.7\cdot10^9$	Phenanthrene	4.51	$\sim7.0\cdot10^8$
Perylene	4.18	$6.4\cdot10^9$	Rhodamine 6G	4.94	$7.5\cdot10^7$
Pyrene	4.21	$\sim2.4\cdot10^9$	Trypaflavine	5.03	$\sim10^7$
1,2-Benzanthracene	4.23	$\sim1.6\cdot10^9$	Pyronine G	5.31	
Tetracene	4.37	$\sim1.8\cdot10^9$	Phenosafranine	5.54	

Calculation of the critical energy transfer radius for the cases presented in Table 1 yields $R_0^{theor} \leqslant 10$ Å§. The mean square diffusion distance during the lifetime of

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§The values of R_0^{theor} quoted previously[10] are somewhat too high.

the excited state ($\sqrt{\bar{r}^2}$), amounting to 40–70 Å, exceeds $3R_0^{\text{theor}}$, which leads to a linear variation of q_0/q with the acceptor concentration C_A. In order to compare the experimental results with the theory of the dipole–dipole energy transfer in liquid solutions, a study was made[17] of the quenching of the fluorescence of various dyes by Nd^{3+} ions. Table 3 presents some of the systems investigated. The distances of closest approach between the interacting molecules ($R_{\min}$) were calculated by the summation of their radii, obtained from their molar volumes (V_M) assuming spherical symmetry. The diffusion rates were also calculated from the V_M by the familiar empirical formula of Wielke and Change[18]. The values of k_t^{theor} were obtained with the aid of a computer from these values of the parameters on the basis of the theory of dipole–dipole energy transfer developed by Rozman and coworkers for liquid solutions[19]. It is noteworthy that very similar values of k_t^{theor} were also obtained by calculations based on the Galanin–Frank[20] and Tunitskii–Bagdasar'yan[21] theories corresponding to the case of "total mixing" or "infinite" diffusion coefficients.

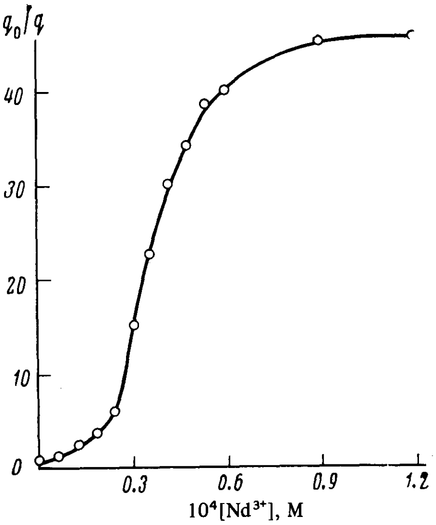

Figure 2. Dependence of the quenching of the eosin fluorescence ($C = 3.0 \times 10^{-5}$ M) on the Nd^{3+} concentration in dimethyl sulphoxide at 293 K under conditions corresponding to the formation of solvated ion pairs.

This is due to the low viscosity of acetone and the low value of R^{theor}. Table 3 shows that the experimental values of k_q for dyes exceed somewhat the values calculated theoretically. For rubrene, k_q and k_t^{theor} are virtually identical. Possibly the energy transfer for dyes with active groups is influenced by the chemical electron donor–electron acceptor interactions. The occurrence of such interactions promotes a more effective penetration of energy donors into the solvation shell of Nd^{3+}, i.e. decreases $R_{\min}$. The fluorescence of other aromatic hydrocarbons (phenanthrene, anthracene, 1,4-benzanthracene, and pyrene) is quenched by Nd^{3+} much less effectively ($k_q > 6 \times 10^8$ litre mole^{-1}s^{-1}) owing to the low value of its overlap integral ($J_0 < 0.06 \times 10^{17}$) with the absorption spectrum of this ion.

Table 3. The quenching of the fluorescence of organic compounds by $Nd(NO_3)_3.6H_2O$ in acetone (293 K, in air; $k_d = 2.1 \times 10^{10}$ litre mole^{-1}s^{-1})[17].

Donor	$10^9\tau_0^{\text{fl}}$*, s	$10^{-10}k_q$, litre mole^{-1} s^{-1}	$10^{17}\cdot J_0$	q_0^{fl}	R_0^{theor}, Å	$10^{-10}k_t^{\text{theor}}$**, litre mole^{-1} s^{-1}	k_q/k_t^{theor}
Magdala Red	4.8	1.6	4.25	0.77	13.3	0.42	3.8
Quinoline Red	6.4	1.6	4.05	0.76	13.2	0.33	4.8
Rhoduline Bright Red B	2.9	1.6	3.71	0.57	12.4	0.47	3.6
Isoquinoline Red	6.3	1.4	3.86	0.87	13.4	0.36	3.9
Rhoduline Red	3.0	1.4	3.11	0.63	12.2	0.45	3.1
Phenosafranine	3.2	1.4	2.98	0.37	11.1	0.27	5.2
Safranine T	3.4	1.1	3.01	0.24	10.4	0.16	6.9
Rubrene	7.4	0.14	2.80	0.71	12.3	0.15	0.9

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*The measurements of τ_0 for the fluorescence of these compounds were kindly carried out by V. Veselova on a GOI phase fluorimeter.

**The theoretically calculated rate constants for the energy transfer.

In moist acetone, where the first studies on the quenching of the fluorescence by lanthanide ions were performed, the lanthanide ions exist in the form of the neutral complexes $Ln^{3+}(NO_3^-)_3.4(5)H_2O$.[22] On the other hand, Shakhverdov showed recently[23] that, when the energy transfer takes place in water, dimethylformamide, dimethyl sulphoxide, and other solvents which are powerful electron donors (in which lanthanide ions exist in the form of triply charged complexes with neutral solvent molecules and the dyes are also employed in the form of charged ions), then such transfer is influenced significantly by the electrostatic repulsive or attractive forces between the energy donor and acceptor.

2. Energy Transfer as an Indicator of a New Type of Ion Pair (Dye–Lanthanide Ion)

In a study of the influence of the solvent on energy transfer from anionic dyes [eosin(2–)] to lanthanide ions, Shakhverdov[23] found that in such a system one can observe several types of interaction between the energy donor and acceptor. Each of these types is clearly manifested in the characteristic dependence of the fluorescence quenching on the concentration of lanthanide ions and in the absorption spectra of the dyes. The measurements made it possible to discover three cases: (1) The quenching of the fluorescence of the donor varies non-linearly with the concentration of lanthanide ions, the absorption spectrum of the dye remaining unchanged. (2) The quenching of the fluorescence increases rapidly at lanthanide concentrations comparable to the concentration of the dye, after which it reaches saturation and remains constant (in the range of C_A from 10^{-4} to 10^{-2} M and above with $C_D \simeq 10^{-5}$ M; see Fig. 2). At the same time there is some enhancement of the absorption (by a factor up to 1.2) or a slight bathochromic shift (< 10 nm) of the absorption band. (3) The donor fluorescence is completely quenched even by low concentrations of the acceptor of the order of $C_A \simeq C_D$ and appreciable changes are observed in the absorption spectrum of the dye.

It was found that two fundamental characteristics of the solvent, namely the dielectric constant ϵ and the donor number *DN* as defined by Gutman[24], are of decisive importance for the type interaction between the dye and the lanthanide ion. The first type includes solvents with high values of ϵ or *DN*, for example formamide and water, and the second includes solvents with moderate values of ϵ and fairly high values of *DN* (glycerol, ethylene glycol, methyl and ethyl alcohols, pyridine, dimethylformamide, and dimethyl sulphoxide). The third class of solvent includes moist acetonitrile and acetone (low values of *DN* and moderate values of ϵ).

Since the energy donor and acceptor have charges of opposite signs (2- and 3+), they can remain free (I) or can form various types of solvent-separated (II) or contact (III) ion pairs as well as covalent complexes (IV):

$$\underset{(I)}{D^{2-}+A^{3+}} \rightleftharpoons \underset{(II)}{D^{2-}|\text{solvent}|A^{3+}} \rightleftharpoons \underset{(III)}{D^{2-},A^{3+}} \rightleftharpoons \underset{(IV)}{D^{2-}:A^{3+}}. \tag{3}$$

It was natural to relate the observed behaviour of the system to the above scheme. Indeed, for high values of ϵ and *DN*, the attraction between ions with different charges is reduced; this does not favour their aggregation. On the other hand, an appreciable decrease of these parameters can lead to the formation of a complex of the dye and the lanthanide ions. It has been suggested[23] that the permanent quenching of the fluorescence of dyes by lanthanide ions in solvents of the second type is due to the energy transfer from $^1\Gamma^*$ states of the dye to the acceptor within ion pairs. This hypothesis is confirmed by the observation of the eosin-sensitised luminescence of Nd^{3+} in dimethylformamide and d_6- and h_6- dimethyl sulphoxide. The correlation between k_q and $\int_0$ for four ions absorbing in the region of the fluorescence of D ions (Table 4) permits the conclusion that the mechanism of energy transfer in the postulated ion pairs is of the dipole–dipole (*dd*) type. The slightly higher value of $k_q/\int_0$ for Nd^{3+} compared with other ions may be due to the contribution to its $\int_0$ via the $^4I_{9/2} \rightarrow {}^4G_{5/2;7/2}$ transitions, which are allowed, being of the quadrupole type.

The observed quenching of fluorescence by non-absorbing ions may be explained by electron phototransfer within ion pairs. It is known[12,25] that Eu^{3+}, Sm^{3+}, and Yb^{3+} ions are capable of reversible photochemical reduction to the bivalent state and Ce^{3+}, Dy^{3+}, and Tb^{3+} ions are capable of reversible photochemical oxidation. Electron phototransfer processes with participation of free Eu^{3+} and Ce^{3+} ions have been investigated by Shakhverdov[11]. When an excess of $Gd(NO_3)_3$ is added to a solution of eosin in dimethylformamide, the fluorescence of which has been quenched by $Nd(NO_3)_3$, the eosin fluorescence is re-established and can be restored almost to the initial level. The effect of $Gd(NO_3)_3$ can be explained by the displacement of Nd^{3+} as the counterion from the [eosin(2-) ... Nd^{3+}] ion pair and its replacement by Gd^{3+}, which hardly quenches the fluorescence of the dye. The composition of the ionic associated species has been determined by spectrophotometrical analytical methods[26] [the isomolar series (continuous variations) and molar ratios methods] in dimethyl sulphoxide at 293 K (it was indeed found to be 1 : 1) together with its instability constant, which proved to be 9.4×10^{-7} mole litre^{-1}.

Assuming a *dd* energy transfer mechanism for the quenching of the fluorescence of eosin in ion pairs with Nd^{3+}, Ho^{3+}, Pr^{3+}, and Er^{3+}, the distances between the ions in such pairs were calculated by the Förster–Galanin theory[23,26]. Values ranging from 6.2 to 7.3 Å were obtained (Table 4), i.e. approximately equal to the sum of the radii of the dye and the solvated lanthanide ion. We obtained similar values of *R* (R_{min}) in a study of the reverse energy transfer from Tb^{3+} to eosin in water, where the ions are not bound in pairs[27]. Thus the distance between the components of the ion pair can be determined by studying the energy transfer, which is of considerable interest.

Table 4. The quenching of the fluorescence of eosin (2-) in ion pairs with lanthanide ions in dimethylformamide (293 K; $C_{eosin} \simeq 5 \times 10^{-6}$ M; $\tau_0^{fl} = 3.9 \times 10^{-9}$ s; $q_0^{fl} = 0.76$)[23].

Quenching agent	q_0/q	k_q, s^{-1}	$10^{18} \int_0$	$10^{-26} k_q \int_0$	*R*, Å
Nd^{3+}	49	$1.23 \cdot 10^{10}$	26.4	4.7	6.2
Ho^{3+}	4.0	$7.7 \cdot 10^{8}$	4.26	1.8	7.3
Pr^{3+}	3.8	$7.2 \cdot 10^{8}$	3.06	2.3	7.0
Er^{3+}	3.1	$5.4 \cdot 10^{8}$	1.99	2.7	6.8
Gd^{3+}	1.1	2.[illegible]$\cdot 10^{7}$	0.00	—	—
La^{3+}	1.0	$<10^{7}$	0.00	—	—
Eu^{3+}	9.7	$2.2 \cdot 10^{9}$	<0.01	>2200	—
Sm^{3+}	2.6	$4.1 \cdot 10^{8}$	0.00	—	—
Yb^{3+}	1.2	$5.1 \cdot 10^{7}$	0.00	—	—
Ce^{3+}	2.4	$3.6 \cdot 10^{8}$	0.00	—	—
Dy^{3+}	2.4	$3.6 \cdot 10^{7}$	0.00	—	—
Tb^{3+}	1.7	$1.8 \cdot 10^{8}$	0.00	—	—

*The first-order rate constants determined from the change in the intensity of the fluorescence of eosin in the presence of lanthanide ions.

We are not aware of data obtained by other methods concerning the possible existence of ion pairs comprising dyes and lanthanide ions¶. The concept of ion pairs is widely used nowadays in the investigation of the interaction of radical-anions and organic carbanions with alkali metal ions[29].

It is noteworthy that the relative extents of quenching of the fluorescence of eosin by lanthanide ions, determined from the decrease of the yield q_0/q and of $\tau_{fl} = \tau_0/\tau$, are not equal. τ was measured with the aid of a phase fluorimeter. $q_0/q = 4.0$ and $\tau_0/\tau = 1.7$ were obtained for Ho^{3+} ions. This difference may be due to both the simultaneous coexistence in solution of several types of ion pairs and to partial dissociation of the ion pairs into individual ions.

The ion pairs formed in aqueous solutions are highly dissociated. The quenching of the fluorescence of eosin by lanthanide ions is in this case slight, is manifested at much higher concentrations than in dimethylformamide and dimethyl sulphoxide ($q_0/q \simeq 4$ for $C_{Nd^{3+}} = 0.04$ M), and is not accompanied by a decrease of τ_0^{fl}. The p*K* values

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¶The presence of ion pairs of another type involving cationic dyes and lanthanide ions, where the interaction takes place via the anions (Cl^-, Br^-) associated with the dye, has been suggested[28] in a study of the NMR shift induced by lanthanides.

for the 1 : 1 eosin–Nd^{3+} ion pairs in water, measured by the equilibrium shift method modified to allow for quenching of luminescence, were found to be 1.64, 1.79, 1.96, 2.13, and 2.32 at pH 5.5 and ionic strengths of 0.48, 0.24, 0.12, 0.06, and 0.03 respectively. Extrapolation to zero ionic strength (using the Davies equation[30]) yields $pK = 2.85$, i.e. $K = 1.4 \times 10^{-3}$ M. It is noteworthy that the spectrophotometric methods do not yield in this case any information, since the formation of eosin–Nd^{3+} ion pairs ($C \leqslant 0.04$ M) is not accompanied by a change in the absorption spectra. The neutralisation of lanthanide ions in aqueous solutions containing eosin following the addition of sodium acetate, sodium sulphate, sodium nitrate, etc. leads to an appreciable decrease in the efficiency of the fluorescence quenching[22]. The anions of the above salts are more likely to form complexes with Ln^{3+} than in eosin. The sequence of the inhibiting effects of the anions is satisfactorily correlated with the stability constants of their complexes with lanthanide ions.

Table 5. Comparison of the calculated (R_0^{theor}) and experimental (R_0^{exp}) critical radii for energy transfer from $Eu(TTA)_3Phen$ to dyes {2 : 1 ethanol–ether; 77 K; $[Eu^{3+}] \simeq 10^{-4}$ M; $\tau_0^{lum} \simeq 0.7$ ms}[31,32].

Acceptor	R_0^{exp}, Å	R_0^{theor}, Å
Aniline Blue	70	72
Brilliant Green	70	72
Cyan Blue	71	71
Turquoise Blue G**	70	70
Victoria Blue 4R	56	67
Victoria Blue R	57	66
Methyl Violet	51	57

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*TTA = thenoyltrifluoroacetonate and Phen = 1,10-phenanthroline.

**The above dye (Tũrkis blau G) has been incorrectly referred to in some studies[31-33] as "Turkish Blue G".

***The values of R_0^{theor} were calculated on the assumption that $\bar{\Phi} = \sqrt{2/3}$. According to Maksimov and Rozman[37], $\bar{\Phi} = 0.845\sqrt{2/3}$ for solid solutions, but we were unable to correct R_0^{theor} because q_{OD} was somewhat too high.

3. Energy Transfer from Lanthanide Ions to Dyes in Solutions

Ermolaev and Shakhverdov[31-33] investigated the non-radiative energy transfer from excited lanthanide ions (Eu^{3+}, Tb^{3+}) to dyes in solid and liquid solutions when the luminescence spectra of Eu^{3+} and Tb^{3+} overlapped the intense absorption bands of the dyes. The lanthanide ions were used in the form of complexes with organic ligands and also as their nitrate salts. It was shown that the addition of dyes (anionic and cationic) to the solid solutions containing Eu^{3+} leads to a decrease of the yield and a shortening of τ—the luminescence time of the ion. The quenching was accompanied by the appearance of the sensitised fluorescence of the dyes. By comparing the concentrations of the acceptor which correspond to the quenching of the fluorescence by a factor of two and the $\int_0$ for the spectra, it was shown[31] that the quenching is due to the inductive-resonance dipole–dipole energy transfer. In conformity with the Főrster–Galanin theory, the relative decrease of τ was smaller than the relative decrease of the luminescence yield. At the same time, deviations of the rate of decay of the luminescence from the exponential relation were observed for the quenched solid solutions. The calculated dependence of the efficiency of the quenching of the Eu^{3+} luminescence on the concentration of acceptors and the luminescence decay law for dipole–dipole energy transfer in Refs. 34–36 agreed satisfactorily with experimental data. Table 5 presents several values of the theoretical critical energy transfer radii and compares them with the R_0^{exp}. Evidently the agreement for the first four pairs is satisfactory; the poorer agreement for the last three combinations we believed to be caused by the greater tendency of these dyes towards dimerisation under the experimental conditions.

Thus one can claim with confidence that the quenching of the luminescence of lanthanide ions by dyes in solid solutions is due to *dd* energy transfer when there is no chemical interaction between them leading to a change in the absorption spectra:

$$^1(Ln^{3+})^* + {}^1A \rightarrow Ln^{3+} + {}^1A^* \,, \tag{10}$$

where ^1A and $^1A^*$ are the molecules of the energy acceptor (dye) in the ground and excited singlet states. The energy level diagram for energy transfer of this type is illustrated in Fig. 3.

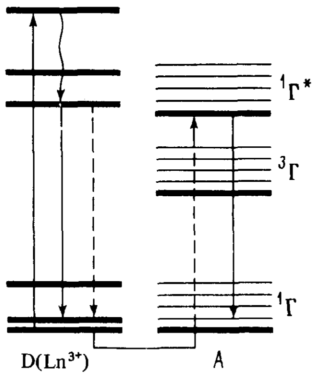

Figure 3. Schematic illustration of the electronic levels in the energy transfer from lanthanide ions to organic dyes with excitation of the singlet excited levels of the latter.

In order to investigate the influence of diffusion on the above energy transfer a study was made of the quenching of the luminescence of Tb^{3+} compounds in liquid solutions[32,33]. The values of $\int_0$ were varied widely (within the limits of three orders of magnitude); compounds with $\int_0 = 0$ were also used. It was noted that τ_0^{lum} decreased, but, in contrast to the solid solutions, the quenching of the Tb^{3+} luminescence remained exponential. The absolute quenching rate constants k_q were obtained from the Stern–Volmer relations between τ_0^{lum}/τ^{lum} and C_A. It was found that the values of $k_q/\int_0$ remained approximately the same, which provided evidence for the assumption that in liquid solutions the quenching of the luminescence of lanthanide ions is caused also by *dd* energy transfer. For low values of $\int_0$ and $\int_0 = 0$, exchange interactions leading to the excitation of the triplet states of the organic molecules† contributed to the quenching of the luminescence. However, the rate constants for such processes were low ($\leq 3 \times 10^5$ litre mole^{-1}s^{-1}) compared with energy transfer to the singlet states.

Table 6 presents data obtained by Shakhverdov and Ermolaev[33] for the quenching of the $Tb(Sal)_3$ luminescence by a number of dyes‡. The measured k_q were compared with the values calculated from the theory of *dd* energy transfer in the presence of diffusion[19] and reasonably satisfactory agreement between them was obtained, bearing in mind the uncertainty in the parameter R_{min}. Table 6 also lists the values of R^{theor}_{min} calculated for the condition that $k_q = k^{theor}_t$. The discrepancy between k_q and k^{theor}_t for $Tb(NO_3)_3$ is greater than for $Tb(Sal)_3$:[33] in the latter case, additional electron donor–electron acceptor interactions between Tb^{3+} and the dyes probably contribute to the energy transfer. Analysis of the results showed that energy transfer from lanthanide ions can be described satisfactorily in terms of the conclusions derived from theories based on the case of infinite diffusion coefficients (Galanin[38], Galanin-Frank[20], Tunitskii–Bagdasar'yan[21]). The mean square diffusional distance ($\sqrt{\bar{r}^2}$) during the period τ_{OD} is approximately 2×10^4 Å, which greatly exceeds R_0^{theor}. This is responsible for the exponential decay of the luminescence of the quenched solutions and for the linearity of the relation $\tau_0/\tau = q_0/q = f(C_A)$. By altering the temperature, it is possible to vary $\sqrt{\bar{r}^2}$. Thus energy transfer from lanthanide ions to dyes constitutes a convenient model for the investigation of the influence of diffusion and dipole–dipole energy transfer.

Table 6. The quenching of the luminescence of $Tb(Sal)_3^*$ by dyes {methanol; 293 K; $[Tb^{3+}] = 2 \times 10^{-4}$ M; $\tau_0^{lum} = 1.0 \times 10^{-3}$ s}[33].

Acceptor	$10^{-6}k_q$, litre mole^{-1} s^{-1}	$10^{14}\cdot\int_0$	$10^{-20}\cdot k_q/\int_0$	R_0, Å	R_{min}, Å	$10^{-6}k_t^{theor}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{theor}}$	k^{theor}_{min}, Å
Fuchsine	309	57.6	5.4	60.9	9.7	139	2.2	7.5
New Fuchsine	216	40.6	5.3	57.5	9.9	92.8	2.3	7.5
Safranine T	117	19.4	5.9	51.0	9.7	48.2	2.4	7.3
Magdala Red	83.4	15.6	5.4	49.0	10.1	33.5	2.5	7.6
Acridine Orange	12.9	2.20	5.9	35.3	9.5	5.62	2.3	7.3
Coryphosphine	10.7	1.34	8.0	32.6	9.4	3.62	2.9	6.6
Chrysoidine	9.7	1.14	8.5	31.9	9.2	3.37	2.9	6.5

* Sal = salicylate anion (Ed. of Translation).

The change in the overall diffusion coefficients from 10^{-5} cm^2 s^{-1} to infinity for the overall energy transfer from lanthanide ions to dyes ($R_0^{theor} \simeq 60$ Å) has no effect whatever on the transfer rate constant. This greatly facilitates the study of the influence of the chemical nature of the solvent on the energy transfer. Our data for energy transfer from $Tb(NO_3)_3$ to fuchsin are presented in Table 7. In order to compare experiment with theory, the values of R_0^{theor} were calculated in all cases from the $\int_0$ and q^{fl}_{OD}. We obtained the theoretical values of k^{theor}_t from the Tunitskii–Bagdasar'yan formula[21] [see also Eqn. (6) in Ref. 1], assuming that $R_{min} = 8$ Å. The influence of Coulombic interaction on the energy transfer between fuchsin and Tb^{3+} ions, which are positively charged (the 1+ ... 3+ system), is in this case small (see subsection 4) and was disregarded.

Table 7. The quenching of the luminescence of $Tb(NO_3)_3$ by fuchsine in various solvents {$[Tb^{3+}] = 0.02$ M; 293 K}.

Solvent	ε	*DN*	$10^{-8}k_q$, litre mole^{-1} s^{-1}	R_0, Å	$10^{-8}k_t^{theor}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{theor}}$	R^{theor}_{min}, Å
Acetonitrile	38.0	14.1	7.4	51.9	1.0	7.4	4.1
Acetone	20.7	17.0	7.0	54.3	1.3	5.4	4.5
Pyrdine	12.3	33.1*	2.8	46.0	0.52	5.4	4.6
Methanol	31.2	—	4.5	53.1	0.91	4.9	4.8
Water (H_2O)	81.0	18.0	0.86	37.0	0.28	3.1	5.5
Water (96% D_2O)	79.0	—	0.61	46.9	0.23	2.7	5.8
Tributyl phosphate	6.8	23.7	1.4	55.0	0.61	2.3	6.1
Dimethylformamide	36.1	26.6	1.8	56.1	0.95	1.9	6.5
Dimethylsulphoxide	45.0	29.8	0.72	51.7	0.47	1.5	7.0

* The values of *DN* for the solvents were determined by Gutmann[24] relative to $SbCl_5$. For lanthanide ions, coordination via the nitrogen atom is weaker than via the oxygen atom. Thus the value *DN* quoted for pyridine is much too high in relation to other solvents as regards interaction with lanthanide ions.

Comparison of the theory and experiment showed that the efficiency of such transfer (i.e. k_q/k^{theor}_t) decreases with enhancement of the electron-donating properties of the solvent (*DN*) and is independent of ε (see Table 7). The deviation of pyridine from the above series, observed by Ermolaev and coworkers[39,40], is due to the specific features of its interaction with lanthanide ions. The decrease of the ratio k_q/k^{theor}_t with increase of *DN* may be accounted for by the increase of R_{min}. It is known that an increase of *DN* for solvents entails an increase in their solvating capacity in relation to lanthanide ions. This leads to an increase of the size of the first coordination sphere of such ions. Furthermore, in solvents which are powerful electron donors there is also a possibility of a certain degree of order also in the second coordination sphere of the lanthanide ions, which prevents its penetration by dyes. In solvents which are weak electron donors (acetone, acetonitrile), dyes are also apparently capable of becoming incorporated in the first coordination sphere. Indeed, theoretical calculation of R^{theor}_{min} for solvents of this type (on the basis of the condition $k_q = k^{theor}_t$) yields very low values (down to 4.1 Å). Some influence of the *DN* for solvents on the reverse transfer (from dyes to lanthanide ions) has also been noted, but in this case it is masked by the influence of solvent viscosity.

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† See Section III below.

‡ Sal = salicylate anion.

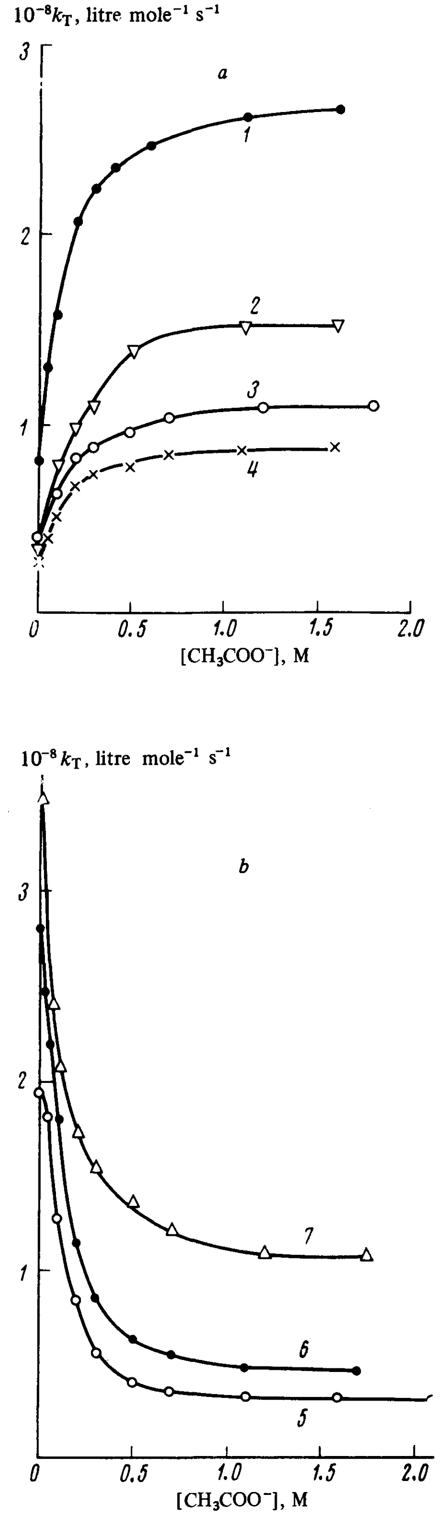

Figure 4. Dependence of the rate constant for the quenching of the Tb^{3+} luminescence (C = 0.03 M) by various dyes in water on the CH_3COONa concentration: *a*) the (3+...1+) system [quenching agent: 1) fuchsine; 2) phenosafranine; 3) new fuchsine; 4) safranine T]; *b*) the (3+...2-) system [quenching agent: 5) acid fuchsine; 6) eosin; 7) erythrosin].

4. The Influence of Electrostatic Interactions of the Donor and Acceptor on the Efficiency of Energy Transfer

We have considered hitherto non-radiative energy transfer mainly between neutral complexes of lanthanide ions and dyes. However, in many solvents lanthanide ions and dyes exist in the form of charged ions. In this case, the rate of non-radiative energy transfer is influenced also by the forces of the electrostatic interaction between the donor and acceptor. Shakhverdov and Bodunov[23,32,41] demonstrated such influence in the energy transfer from the free Tb^{3+} ion in water to anionic (2-) and cationic (1+) dyes, the results being compiled in Table 8, which shows that the efficiency of the quenching of the Tb^{3+} luminescence by dyes (the k_q/J_0 ratio) depends markedly on the sign of the charge of the latter. The interaction of anionic dyes with lanthanide ions is much more effective. To demonstrate the electrostatic nature of the influence of the acceptor charge, sodium acetate (CH_3COONa), whose anions form neutral complexes with Tb^{3+}, was introduced into the solution. This resulted in the opposite effect on the (3+ ... 1+) and (3+ ... 2-) systems. In the former case k_q decreased and in the latter increased (Fig. 4); the values of k_q/J_0 became equal under these conditions. The limiting quenching constants in the presence of sodium acetate (k'_q) and k'_q/J_0 are listed in Table 8.

Table 8. The quenching of the luminescence of $Tb(NO_3)_3$ by organic dyes in water $\{[Tb^{3+}] = 0.03\ M;\ \tau_0^{lum} = 4.5 \times 10^{-4}\ s;\ \tau_0'^{lum} = 7.0 \times 10^{-4}\ s;\ 293\ K\}$[41].

Acceptor	$10^{-7}k_q$, litre mole^{-1} s^{-1}	$10^{-7}k'_q$, litre mole^{-1}s^{-1}	$10^{-20}\frac{k_q}{J_0}$	$10^{-20}\frac{k'_q}{J_0}$	$\frac{k'_q}{k_q}$	$\frac{k_t'^{theor}}{k_t^{theor}}$ (13H$_2$O)	$\frac{k_t'^{theor}}{k_t^{theor}}$ (6H$_2$O)
			(3+...1+) System				
Fuchsine	8.6	26.7	2.8	8.7	3.1	2.8	2.7
Safranine T	2.9	8.6	2.9	8.7	3.0	2.8	2.8
New Fuchsine	3.9	10.8	1.3	3.6	2.8	2.7	2.7
Phenylsafranine	3.6	15.0	2.2	10.4	4.7	2.9	2.8
Rhoduline Red B	0.71	2.3	1.1	3.7	3.2	2.7	2.7
			(3+...2-) System				
Acid Fuchsine	19.5	3.2	34.8	5.7	0.16	0.47	0.26
Eosin	28.4	4.7	16.3	2.7	0.16	0.42	0.22
Erythrosin	35.5	10.5	20.1	6.0	0.29	0.45	0.23
Bengal Rose	59.7	14.0	20.0	4.7	0,23	0.45	0.24

The results of the above experiments were compared with theoretical computer calculations based on Bodunov's theory[42,43], taking into account the influence of the electrostatic interaction between the ions on the dipole-dipole energy transfer. The calculations were performed for two cases, differing in the size of the hydration shell of Tb^{3+}. In the first case, it was assumed that the entire hydration shell (known to comprise approximately 13 water molecules according to diffusion data) determines the value of R_{min}. In the second case, account was taken only of the immediate environment of Tb^{3+} (six water molecules). In the calculations, the change in R_0^{theor}, R_{min}, and τ_0^{lum} on formation of Tb^{3+} complexes with CH_3COO^- was also taken into account. This leads in all cases to an increase of $k_t'^{theor}/k_t^{theor}$ by factors of 1.8

and 1.3 respectively. There was a difference between the absolute values of k_q and k'_q determined experimentally and calculated theoretically. The reason for this is not altogether clear and, as stated above, is apparently due to the solvent. On the other hand, the effect of the electrostatic interactions on the energy transfer is described fairly satisfactorily by the theory[42,43]. Table 8 lists the experimental (k'_q/k_q) and theoretical ($k'^{\text{theor}}_t/k_t^{\text{theor}}$) ratios of the rate constants for the quenching of the Tb^{3+} luminescence by dyes with and without sodium acetate. Evidently, in the system with Coulombic repulsion between the ions (3+ ... 1+), the change in the parameter $R_{\min}$ has no influence whatever on the theoretical rate constant ratio and corresponds to the experimental values of k'_q/k_q. On the other hand, the system with a Coulombic attraction between the ions (3+ ... 2-) is more sensitive to this parameter. The agreement with experiment in this system is found to be better when account is taken of only the first coordination sphere of Tb^{3+}.

5. Energy Transfer from Lanthanide Ions to Organic Radical-Ions

It was of interest to investigate the influence of the multiplicity of the energy states of the energy acceptors on the mechanism of the energy transfer from lanthanide ions. For this purpose, Shakhverdov[44] used for acceptors the radical-cations of aromatic hydrocarbon with a doublet ($^2\Gamma$) ground state. One could then expect the occurrence of an exchange energy transfer, since the Wigner rule (overall spin conservation) holds under these conditions. The experiments were performed in sulphuric acid at 293 K. The quenching of the Tb^{3+} and Eu^{3+} luminescence by three radical-cations was investigated (Table 9). At the same time, experiments were performed with acceptors having a $^1\Gamma$ ground state (the proton complex of tetracene, etc.). In both cases, the experimental results were compared with theory (assuming that $R_{\min}$ = 8 Å). It was shown that the quenching of the luminescence of lanthanide ions by an organic radical is due to *dd* energy transfer. An estimate of the probability of electron phototransfer in such systems showed that it cannot compete with energy transfer. Indeed k_q for the quenching of the Tb^{3+} luminescence in sulphuric acid by one of the most powerful electron acceptors (Ce^{4+} ions) proved to be only ~ 1.2×10^6 litre $\text{mole}^{-1}\text{s}^{-1}$. In the quenching of the Eu^{3+} luminescence by powerful organic electron donors (diphenylamine and triphenylamine) and in the quenching of the Tb^{3+} luminescence by electron acceptors (chloranil, bromanil, *p*-benzoquinone, and *sym*-trinitrobenzene), the values of k_q are likewise low. Thus $k_q \leq 2.2 \times 10^6$ litre $\text{mole}^{-1}\text{s}^{-1}$ for the quenching of the Tb^{3+} luminescence (in methanol) and $k_q \leq 4.8 \times 10^5$ litre $\text{mole}^{-1}\text{s}^{-1}$ for Eu^{3+} (in acetone). The change in the multiplicity of the ground state of the acceptors (from $^1\Gamma$ for dyes to $^2\Gamma$ for radicals) did not therefore lead to a change in the mechanism of the energy transfer.

III. THE EXCHANGE-RESONANCE ENERGY TRANSFER

The exchange-resonance energy transfer between the donor and the acceptor requires overlap of their electron clouds[45,46], which is also needed for the formation of a covalent bond between them. Indeed, a definite correlation can be established in many instances between energy transfer and complex formation. It is particularly pronounced for the interaction of triplet ketones with lanthanide ions and of excited lanthanide ions with aromatic ketones, leading to energy transfer from the excited triplet levels of the latter. Energy transfer involving lanthanide ions to and from the triplet level of organic molecules takes place via the exchange-resonance mechanism[47-49]. As will be shown below, this is why the study of this type of energy transfer has proved particularly fruitful in the development of methods for the investigation of complex formation in solutions.

Table 9. The quenching of the luminescence of lanthanide ions in 95% sulphuric acid at 293 K[44].

Acceptor	$10^{-7}k_q$ litre $\text{mole}^{-1}\text{s}^{-1}$	$10^{14}\cdot J_0$	$10^{-20}\cdot \frac{k_q}{J_0}$	R_0, Å	$10^{-7}k_t^{\text{theor}}$, litre mole^{-1} s^{-1}	$\frac{k_q}{k_t^{\text{theor}}}$	$R_{\min}^{\text{theor}}$, Å
Tb^{3+} donor (C = 0.01 M, $\tau_0 = 2.4 \times 10^{-3}$ s)							
$\text{Perylene}^{\cdot+}$	12	25.8	4.7	54	5.0	2.4	6.0
9,10-Diphenyl-$\text{anthracene}^{\cdot+}$	3.6	6.7	5.4	13	1.3	2.8	5.8
$\text{Tetracene}^{\cdot+}$	0.65	1.5	4.3	33	0.29	2.2	6.1
(Tetracene)H^+	1.9	3.5	5.4	39	0.66	2.9	[illegible].7
Eu^{3+} donor (C = 0.01 M, $\tau_0 = 1.2 \times 10^{-3}$ s)							
9,10-diphenyl-$\text{anthracene}^{\cdot+}$	7.2	15.6	4.6	48	4.8	1.5	7.0
$\text{Perylene}^{\cdot+}$	5.7	7.6	7.5	42	2.3	2.5	6.0
$\text{Tetracene}^{\cdot+}$	2.9	5.6	5.2	40	1.7	1.7	6.
(Tetracene)H^+	3.7	7.4	5.0	42	2.3	1.6	6.8

1. Energy Transfer from the Triplet States of Organic Molecules to Lanthanide Ions

(a) Solid solutions. The first experiments on these lines were published by Smaller et al.,[50] who observed a marked decrease of the amplitude of the ESR signal of the triplet molecules of perdeuteronaphthalene in a 9 : 1 methanol–water solution at 77 K in the presence of Gd^{3+} ions. They believed that the mechanisms of this quenching involved the intercombination transition $^3\Gamma \rightsquigarrow \Gamma_0^1$ catalysed by the paramagnetic ion. Indeed the Gd^{3+} ion has a high magnetic moment (8.2 μ_B). In addition, they also observed a non-rigorous correlation between the rate of quenching of the triplet state and the magnetic moments of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, and Gd^{3+} ions.

Breuninger and Weller[51] recently investigated the influence of the addition of Gd^{3+}, La^{3+}, and Tb^{3+} ions on the luminescence of perdeuteronaphthalene and triphenylene in a 9 : 1 methanol–water solid solution at 77 K. The fluorescence of naphthalene and triphenylene is not quenched by lanthanide ions up to a concentration of the latter of 0.5 M. The phosphorescence of both hydrocarbons is quenched by Tb^{3+} ions, but not Gd^{3+} and La^{3+} ions. They showed that the decreased amplitude of the ESR signal of triplet perdeuteronaphthalene in the presence of Gd^{3+}, observed by Smaller et al.,[50] is due exclusively to the broadening of the ESR lines of the triplet molecules and not to a decrease in their concentration.

Breuninger and Weller[51] explained the quenching of the phosphorescence of organic molecules by Tb^{3+} (and transition metal) ions as a consequence of non-radiative energy transfer. The occurrence of energy transfer is confirmed by the observation of the triphenylene-sensitised Tb^{3+} luminescence. The energy transfer in the case of Tb^{3+} has an exchange-resonance mechanism; this is supported by the exponential variation of the quenching of the phosphorescence (q_{OD}/q_D) with the concentration of the energy acceptor (Tb^{3+}) and by the approximately tenfold difference between the slopes of the q_{OD}/q_D and τ_{OD}/τ_D curves as a function of Tb^{3+} concentration. The critical radii R_0 and ρ^{-1}§ for the transfer from perdeuteronaphthalene and triphenylene to Tb^{3+} are respectively 11.0 Å and 0.10 for perdeuteronaphthalene and 13.6 Å and 0.14 for triphenylene. The values of R_0 and the ratios of the slopes obtained for the systems investigated are close to the analogous quantities for the triplet–triplet energy transfer between organic molecules in solid solutions via the exchange-resonance mechanism[46,52,53].

The high efficiency of energy transfer from the $^3\Gamma$ states to the Tb^{3+} ion has been explained[51] by the incorporation of the energy donors in the solvation shell of the ion and the formation of complexes. We believe that this explanation is not very probable for the system investigated, since the inner coordination shell comprises polar water and alcohol molecules and their displacement by non-polar aromatic hydrocarbon molecule is unlikely.

The quenching of the benzoquinone phosphorescence by lanthanide ions in solid alcohols at 77 K was investigated by Gevorkyan[54]. An exponential relation was observed between the quenching and the concentrations of Nd^{3+}, Eu^{3+}, and Tb^{3+} ions. The critical transfer distances are 13.0 Å for Nd^{3+}, 12.0 Å for Eu^{3+}, and 11.0 Å for Tb^{3+}. The ratio ρ is close to 10 for quenching by Eu^{3+} and Tb^{3+} and of the order of 4–6 for quenching by Nd^{3+}. We suggest that in the case of Eu^{3+} and Tb^{3+} the exchange-resonance mechanism is decisive, while quenching by Nd^{3+}, which has more intense absorption bands, involves both exchange-resonance and inductive-resonance energy transfer mechanisms.

The energy transfer from two ketones (methyl 2-naphthyl ketone and 2-fluorenyl methyl ketone) to Eu^{3+} and Tb^{3+} ions in solid solutions (1 : 4 methanol–ethanol) at 77 K has been investigated by Minn et al.[55,56] They established the occurrence of energy transfer from the decrease in the decay time and in the intensity of the phosphorescence of the ketones in the presence of lanthanide ions and also from the appearance of the sensitised Eu^{3+} and Tb^{3+} luminescence. Their quantitative data are in poor agreement with modern ideas concerning any of the known mechanisms of non-radiative energy transfer in solid solution. The effective Bohr radii quoted by the authors[55,56] for the system investigated, namely $L = 4.5$–20 Å, also appear to be extremely doubtful, since $L < 2$ Å even for the triplet–triplet energy transfer between two aromatic molecules and the rate of decrease of the electron density for the 4*f* shell of the lanthanide ion must be greater than the rate of decrease of the π-electron density. The mechanism of energy transfer from aromatic ketones to lanthanide ions in solid solutions requires additional investigation.

(b) Liquid solutions. The role of complex formation. Porter and Wright[57] observed the quenching of the triplet state of naphthalene by neodymium ions in ethylene glycol at 298 K; $k_q = 4 \times 10^5$ litre $mole^{-1} s^{-1}$, which is lower by three orders of magnitude than the diffusion rate constant under the same conditions ($k_d = 3.7 \times 10^8$ litre $mole^{-1} s^{-1}$). It was suggested that the effect is due to the intercombination degradation of the triplet molecule to the ground state catalysed by the lanthanide ion:

$$^3D + {^nLn^{3+}} \rightsquigarrow {^1D} + {^nLn^{3+}}. \qquad (11)$$

Matovich and Suzuki[58] and other investigators[59–64] demonstrated the sensitisation by the solvent of the luminescence of Eu^{3+}, Sm^{3+}, Tb^{3+} and Dy^{3+} ions dissolved in aromatic ketones. The phenomenon is due to the non-radiative energy transfer from the lowest triplet levels of the ketones to lanthanide ions:

$$\begin{aligned} &^3D + {^nLn^{3+}} \rightarrow {^1D} + {^m(Ln^{3+})^*}; \\ &^m(Ln^{3+})^* \rightarrow {^nLn^{3+}} + h\nu_{s.l.} \end{aligned} \qquad (12)$$

The fact that the intramolecular energy transfer in complexes of lanthanide ions with organic compounds observed previously[65–68] did not occur under these conditions was demonstrated by the following findings: (1) the coincidence of the absorption spectra of the ketone and the ketone–lanthanide ion system in the range 300–400 nm, where lanthanide ions do not exhibit an absorption comparable to that of ketones; (2) by the disappearance of the sensitised luminescence on freezing. The intensity of the sensitised luminescence of lanthanide ions in ketones increased with increase in the temperature of the solution. On the other hand, Faidysh and coworkers[69] observed a decrease in the intensity of the sensitised luminescence of $Eu^{3+}(NO_3^-)_3$ dissolved in benzophenone with increase of temperature and the sensitised luminescence did not disappear even at 77 K. A complication which prevented an unambiguous interpretation of these relations[58,66] is the migration of the energy of the triplet excitation via the molecules of the aromatic ketones until their capture by the lanthanide ion. Zolin and coworkers[70–72] extended the range of energy donors by sensitising the lanthanide ions with dyes and certain heteroaromatic compounds.

Ermolaev and coworkers[73–78] investigated the kinetics of the energy transfer from aromatic ketones with lowest triplet states of the n, π^* and π,π^* types to lanthanide ions in solutions. The diffusional mechanism of energy transfer and the involvement in the latter of the lowest triplet state of ketones were demonstrated by the method involving competition between the transfer to the lanthanide ion and the triplet–triplet transfer of energy to the acceptor (see Scheme 1 below).

The study of the dependence of the intensity of the benzophenone-sensitised luminescence of Eu^{3+} on its concentration and on the concentration of the triplet energy acceptor (naphthalene) showed that (1) the transfer takes place from the lowest triplet level of the ketone (see Fig. 5), (2) the rate of energy transfer is proportional to the concentration of the ion and independent of the concentration of the ketone, and (3) the quenching of the benzophenone-sensitised luminescence of the lanthanide ion (Eu^{3+}) by the triplet energy acceptor (naphthalene) obeys the Stern–Volmer relation and it follows from the slope of the linear plot that the rate constant for the energy transfer from the ketone to Eu^{3+} in acetone is almost two orders of magnitude lower than the diffusion rate constant k_d and the conclusion reached by Heller and Wasserman[62] and Filipescu and Mushrush[79] that $k_t = k_d$ for the solvent is therefore incorrect. The later conclusion that $k_t \ll k_d$ was confirmed by Wagner and Schott[80], using the same method, and by Ermolaev and Tachin[74], using the method of flash photoexcitation, from the decay of the triplet–triplet

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§ $$\rho = \lim_{C_A \to 0} \frac{d(q/q_0)}{dC_A} \frac{d(\tau/\tau_0)}{dC_A}.$$

absorption. Table 10 lists the rate constants for the energy transfer from triplet ketones to Eu^{3+}. It shows that the rate constant for the intermolecular transfer in moist acetone for aromatic ketones without substituents in the benzene rings is an order of magnitude higher in the case of ketones with the lowest triplet state of the n,π^* type compared with ketones in which this state is of the π,π^* type. The introduction of electron-accepting substituents into the benzene rings (in our case halogens) greatly decreases the value of k_t.

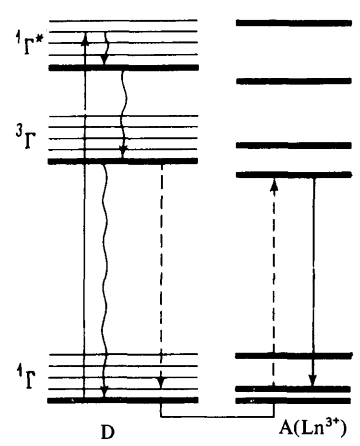

Figure 5. Schematic illustration of the electronic levels in the energy transfer from organic molecules in the triplet state ($^3\Gamma$) to lanthanide ions.

Table 10. The rate constants for the intermolecular energy transfer from the triplet state of ketones to $Eu(NO_3)_3$ in moist acetone at 293 K (according to the data of Ermolaev and Tachin[74] and Morina Sveshnikova[75]).

Ketone	Type and height of $^3\Gamma$ level, cm^{-1}	$10^{-7}k_t$, litre $mole^{-1}$ s^{-1}	Method
Acetophenone	n, π^*; 25 800	20	TT transfer*
Benzophenone	n, π^*; 24 250	60	ditto
γ-Benzoylpyridine	n, π^*; 23 000	[illegible]	»
4-Chloro-4′-methoxybenzophenone	n, π^*; 23 500	15	»
4-Bromobenzophenone	n, π^*; 23 600	3.4	»
4-Chlorobenzophenone	n, π^*; 24 000	2.0	»
4,4′-Dichlorobenzophenone	n, π^*; 24 000	1.3	»
Decafluorobenzophenone	n, π^*; 24 700	0.6	»
Methyl-2-naphthylketone	π, π^*; 20 800	1.2	i.r.**
4-Phenylbenzophenone	π, π^*; 21 225	0.9	»

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*The method based on the competition with the exothermic triplet–triplet energy transfer to the organic acceptor molecule.

**The method of flash photoexcitation based on the influence of Eu^{3+} on the rate of decay of the triplet–triplet absorption in the evacuated solution.

Measurements of the rate constants for the energy transfer from aromatic ketones in the triplet state to different lanthanide ions in moist acetone at 293 K showed that the rate constant for the exothermic energy transfer varies within a range of 1–1.5 orders of magnitude and is in all cases more than 10 times smaller than the rate constant for diffusion in acetone. The attempt to find a correlation between the values of k_t and the overlap integrals of the phosphorescence spectra of the ketone donors with the absorption spectra of the lanthanide ions was unsuccessful[74]. The situation was complicated even further by studies of the influence of solvents and temperature on k_t.[40,77,81] It was established that k_t decreases on passing to solvents characterised by higher Gutmann[24] donor numbers *DN*. k_t in moist acetone, methanol and acetonitrile increases with increase of temperature. Furthermore, Sveshnikova et al.[77] established that, in solvents with low and moderate values of *DN*, there is both intermolecular diffusional and intramolecular energy transfer between aromatic ketones and lanthanide ions. The existence in solution of lanthanide complexes of aromatic ketones is indicated unambiguously by the dependence of the quenching of the luminescence sensitised by ketones on the concentration of the organic triplet energy acceptor. Instead of a straight line of the Stern–Volmer type, which obtains for purely intermolecular transfer, a curve is obtained; this is a result of the summation of two straight lines with different slopes. Examples of such relations are illustrated in Fig. 6 for the quenching by *trans*-stilbene of the luminescence of europium sensitised by 4-ethoxy-4′-methoxybenzophenone.

Scheme I

	Expression for the rate of the process	
$^1K + h\nu_{exc} \rightarrow {}^1K^* \rightsquigarrow {}^3K$	I^{I}_{exc}	(I—1)
$[^1K - Ln^{3+}] + h\nu_{exc} \rightarrow [^1K^* - Ln^{3+}] \rightarrow [^3K - Ln^{3+}]$	I^{II}_{exc}	(I—2)
$^3K \rightsquigarrow {}^1K$	k'_D	(I—3)
$^3K + {}^3O_2 \rightarrow {}^1K + {}^1O_2$	$k^{O_2}_t [O_2]$	(I—4)
$^3K + Ln^{3+} \rightarrow [^3K - Ln^{3+}]$	$k_t [Ln^{3+}]$	(I—5)
$^3K + {}^1A \rightarrow {}^1K + {}^3A$	$k^{TT}_t [^1A]$	(I—6)
$^3K + [^1K - Ln^{3+}] \rightarrow {}^1K + [^3K - Ln^{3+}]$	$k^{TT}_t [^1K - Ln^{3+}]$	(I—7)
$[^3K - Ln^{3+}] \rightarrow {}^3K + Ln^{3+}$	k'_{dis}	(I—8)
$[^3K - Ln^{3+}] \rightarrow [^1K - (Ln^{3+})^*]$	ω_t	(I—9)
$[^3K - Ln^{3+}] \rightarrow [^1K - Ln^{3+}]$	ω_{phch}	(I—10)
$[^3K - Ln^{3+}] + {}^1A \rightarrow [^1K - Ln^{3+}] + {}^3A$	$k^{TT}_t [^1A]$	(I—11)
$[^3K - Ln^{3+}] + {}^3O_2 \rightarrow [^1K - Ln^{3+}] + {}^1O_2$	$k^{O_2}_t [O_2]$	(I—12)
$[^1K - (Ln^{3+})^*] \rightarrow {}^1K + (Ln^{3+})^*$	k_{dis}	(I—13)
$(Ln^{3+})^* \rightarrow Ln^{3+} + h\nu_{s.l.}$	k_i	(I—14)
$(Ln^{3+})^* \rightsquigarrow Ln^{3+}$	k_D	(I—15)

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* ^1K, $^1K^*$, and ^3K denote respectively the organic molecule of the ketone donor in the singlet ground state, the lowest singlet excited state, and the lowest triplet state respectively and ^1A, $^1A^*$, and ^3A are the corresponding quantities for the triplet energy acceptor molecule—the quenching agent for the ketone-sensitised luminescence of the lanthanide ions.

The relations illustrated in Fig. 6 are described approximately within the framework of Scheme I: (a) in the non-excited state of the solution of ketones and lanthanide ions, there is an equilibrium between the ketone–Ln^{3+} complexes $[^1K-Ln^{3+}]$ and solvated ketones (^1K) and we have $[^1K]+[^1K-Ln^{3+}] = C_K$, where C_K is the overall concentration of the ketone in solution. Under the experimental conditions, $[^1K-Ln^{3+}] \ll [Ln^{3+}]$; (b) the energy transfer from the triplet ketone to the lanthanide ion can take place either within the complex with a first-order rate constant ω_t (s^{-1}) when light is absorbed by the complex (I^{II}_{exc}) or intermolecularly in the encounter between the triplet ketone and the lanthanide ion or the complex when light is absorbed by the free ketone ($I^{\mathrm{I}}_{\mathrm{exc}}$).

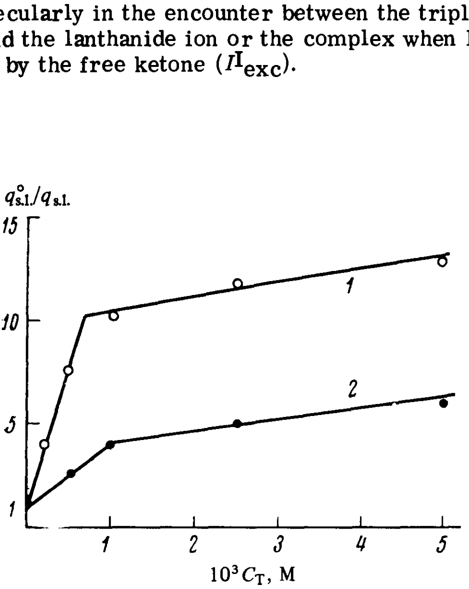

Figure 6. The quenching of the 4-ethoxy-4'-methoxybenzophenone-sensitised (C = 0.01 M) Eu^{3+} luminescence by *trans*-stilbene (concentration C_T) in acetone without O_2 at 293 K; λ_{exc} = 365 nm; Eu^{3+} concentration (M): 1) 0.0128; 2) 0.05.

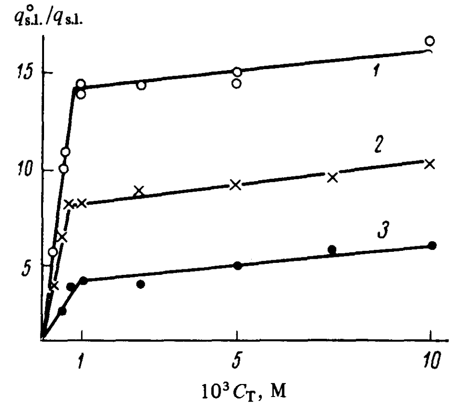

Figure 7. The influence of temperature on the quenching of the 4-methoxybenzophenone-sensitised (C = 0.01 M) Eu^{3+} luminescence (C = 0.05 M) by *trans*-stilbene in acetonitrile at different temperatures (K): 1) 233; 2) 273; 3) 293.

We shall now consider the concentration dependence of the intensity of the sensitised luminescence $I_{\mathrm{s.l.}}$ which follows from Scheme I. The ratio of $I^{\mathrm{I}}_{\mathrm{exc}}$ and $I^{\mathrm{II}}_{\mathrm{exc}}$ depends on the concentrations of the complexes and the free ketone in solution and their extinction coefficients at the wavelength of the exciting light. k'_{d} is the rate constant for the deactivation of the triplet ketone in the de-aerated solution (I-3); (I-4) represents the quenching of the triplet ketone by oxygen; (I-5) is the reaction involving the incorporation of the triplet ketone in the first coordination sphere of the ion; (I-6) and (I-11) represent the exothermic energy transfer from the triplet ketone to the triplet energy acceptor introduced into the solution, the rate of this process being limited by diffusion ($k^{\mathrm{TT}}_{\mathrm{t}} = k_{\mathrm{d}}$); (I-7) is the energy transfer from the triplet ketone to the complex; (I-8) is the dissociation of the triplet complex into the triplet ketone and the non-excited lanthanide ion. The very small temperature dependence of the quenching of the luminescence of the complexes shows that the dissociation process may be neglected compared with the intramolecular energy transfer [ω_{t}, (I-9)] and the photochemical reaction within the complex [ω_{phch}, (I-10)], i.e. $\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} \gg k'_{\mathrm{dis}}$. The quenching of the luminescence of the complex by oxygen (I-12) is also not observed and $\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} \gg k'_{\mathrm{dis}} + k^{\mathrm{O_2}}_{\mathrm{t}}[O_2]$. The lifetime of the luminescent lanthanide ion is long and there is sufficient time for the dissociation of the complex (I-13). Reactions (I-14) and (I-15) correspond to the processes involving the emission of the sensitised luminescence and the degradation of the electronic excitation energy into heat.

Having chosen the experimental conditions, it is possible to simplify the scheme by neglecting a number of processes. By carrying out experiments in de-oxygenated solutions or by establishing a sufficiently high concentration of Ln^{3+}, it is possible to neglect processes (I-3) and (I-4) compared with (I-5) and (I-6). Furthermore, at a relatively low ketone concentration one can disregard process (I-7) involving energy transfer to the complexes, so that

$$k_{\mathrm{t}}[\mathrm{Ln}^{3+}] + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}] \gg k'_{\mathrm{D}} + k^{\mathrm{O_2}}_{\mathrm{t}}[\mathrm{O_2}] + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{K}-\mathrm{Ln}^{3+}].$$

Under the conditions formulated, namely

$$\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} \gg k'_{\mathrm{dis}} + k^{\mathrm{O_2}}_{\mathrm{t}}[\mathrm{O_2}]$$

and

$$k_{\mathrm{t}}[\mathrm{Ln}^{3+}] \gg k'_{\mathrm{D}} + k^{\mathrm{O_2}}_{\mathrm{t}}[\mathrm{O_2}] + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{K}-\mathrm{Ln}^{3+}],$$

the expression for $q_{\mathrm{s.l.}}$ assumes the following form:

$$q_{\mathrm{s.l.}} = \frac{I^{\mathrm{I}}_{\mathrm{exc}}}{I_{\mathrm{exc}}} \cdot \frac{k_{\mathrm{i}}}{k_{\mathrm{i}} + k_{\mathrm{d}}} \cdot \frac{k_{\mathrm{t}}[\mathrm{Ln}^{3+}]}{k_{\mathrm{t}}[\mathrm{Ln}^{3+}] + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]} \cdot \frac{\omega_{\mathrm{t}}}{\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]} + \frac{I^{\mathrm{II}}_{\mathrm{exc}}}{I_{\mathrm{exc}}} \cdot \frac{k_{\mathrm{i}}}{k_{\mathrm{i}} + k_{\mathrm{d}}} \cdot \frac{\omega_{\mathrm{t}}}{\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} + k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]},$$

where $I_{\mathrm{exc}} = I^{\mathrm{I}}_{\mathrm{exc}} + I^{\mathrm{II}}_{\mathrm{exc}}$. The experimental ratio of the intensity of the sensitised luminescence in the absence of quenching agent $q^0_{\mathrm{s.l.}}$ to the intensity in its presence at a concentration $[{}^1\mathrm{A}]$ is given by the following expression:

$$\frac{q^0_{\mathrm{s.l.}}}{q_{\mathrm{s.l.}}} = \frac{\left(1 + \frac{k^{\mathrm{TT}}_{\mathrm{t}}}{\omega_{\mathrm{t}} + \omega_{\mathrm{phch}}} \cdot [{}^1\mathrm{A}]\right)\left(1 + \frac{k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]}{k_{\mathrm{t}}[\mathrm{Ln}^{3+}]}\right)}{\left(1 + \frac{I^{\mathrm{II}}_{\mathrm{exc}}}{I^{\mathrm{I}}_{\mathrm{exc}} + I^{\mathrm{II}}_{\mathrm{exc}}} \cdot \frac{k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]}{k_{\mathrm{t}}[\mathrm{Ln}^{3+}]}\right)}. \quad (14)$$

Bearing in mind that $\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} \gg k_{\mathrm{t}}(\mathrm{Ln}^{3+})$, one can examine two limiting quenching agent concentration ranges. At low quenching agent concentrations, where $k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]/k_{\mathrm{t}}[\mathrm{Ln}^{3+}] < 1$ and bearing in mind that $k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}] \ll \omega_{\mathrm{t}} + \omega_{\mathrm{phch}}$ and $I^{\mathrm{I}}_{\mathrm{exc}} \simeq I^{\mathrm{II}}_{\mathrm{exc}}$, Eqn. (13) can be replaced by the approximate expression

$$\frac{q^0_{\mathrm{s.l.}}}{q_{\mathrm{s.l.}}} \simeq 1 + \frac{I^{\mathrm{I}}_{\mathrm{exc}}}{I^{\mathrm{I}}_{\mathrm{exc}} + I^{\mathrm{II}}_{\mathrm{exc}}} \cdot \frac{k^{\mathrm{TT}}_{\mathrm{t}}[{}^1\mathrm{A}]}{k_{\mathrm{t}}[\mathrm{Ln}^{3+}]}. \quad (15)$$

This expression simplifies still further when the concentration of stable complexes in the ground state is low, so that $I^{\mathrm{I}}_{\mathrm{exc}} \gg I^{\mathrm{II}}_{\mathrm{exc}}$. Then

$$\frac{q^0_{\mathrm{s.l.}}}{q_{\mathrm{s.l.}}} = 1 + \frac{k^{\mathrm{TT}}_{\mathrm{t}}[^1\mathrm{A}]}{k_{\mathrm{t}}[\mathrm{Ln}^{3+}]}. \qquad (16)$$

On the other hand, at high quenching agent concentrations, we have $I^{\mathrm{I}}_{\mathrm{exc}} \simeq I^{\mathrm{II}}_{\mathrm{exc}}$ and $k^{\mathrm{TT}}_{\mathrm{t}}[^1\mathrm{A}]k_{\mathrm{t}}[\mathrm{Ln}^{3+}] \gg 1$. We then obtain a linear variation with $[^1\mathrm{A}]$:

$$\frac{q^0_{\mathrm{s.l.}}}{q_{\mathrm{s.l.}}} = \frac{I^{\mathrm{I}}_{\mathrm{exc}} + I^{\mathrm{II}}_{\mathrm{exc}}}{I^{\mathrm{II}}_{\mathrm{exc}}}\left(1 + \frac{k^{\mathrm{TT}}_{\mathrm{t}}}{\omega_{\mathrm{t}} + \omega_{\mathrm{phch}}}[^1\mathrm{A}]\right). \qquad (17)$$

The intercept which this straight line makes on the ordinate axis makes it possible to estimate $(I^{\mathrm{I}}_{\mathrm{exc}} + I^{\mathrm{II}}_{\mathrm{exc}})/I^{\mathrm{II}}_{\mathrm{exc}}$, i.e. the reciprocal of the fraction of light absorbed by the complexes $[^1\mathrm{K{-}Ln}^{3+}]$ in solution at a given concentration of lanthanide ions and therefore permits the estimation of their stability constants.

Since the rate constant for the exothermic triplet energy transfer is equal to the diffusional constant, $k^{\mathrm{TT}}_{\mathrm{t}} = k_{\mathrm{d}}$, and is calculated from the Vavilov–Debye formula[82,83] $k^{\mathrm{TT}}_{\mathrm{t}} = k_{\mathrm{d}} = 8RT/3000\eta$ (litre $\mathrm{mole}^{-1}\mathrm{s}^{-1}$), the slopes of the linear relations (15)–(17) corresponding to low values of $[^1\mathrm{A}]$ make it possible to determine the rate constant for the intermolecular energy transfer from the triplet ketone to the lanthanide ion (k_{t}), while the slope corresponding to high values of $[^1\mathrm{A}]$ permits the determination of the sum of the constants for the intramolecular energy transfer (ω_{t}) and the photochemical reaction within the complex (ω_{phch}). Knowing the yield of the photochemical reaction[76], it is possible to find ω_{t} from the sum. The values of k_{t}, ω_{t}, and the stability constants β of the complexes $[^1\mathrm{K{-}Ln}^{3+}]$ obtained in the above investigation are listed in Table 11.

Scheme I differs from the schemes usually employed for the description of energy transfer by the allowance for the complex-formation reaction with the lanthanide ions involving the ground and triplet states of the ketone. The validity of the hypothesis of the simultaneous occurrence of two processes involving the formation of ketone–Ln^{3+} complexes is confirmed by the following findings: (1) the relations between $q^0_{\mathrm{s.l.}}/q_{\mathrm{s.l.}}$ and the concentration of *trans*-stilbene presented in Fig. 6 for various ratios of the concentrations of the ketone and the lanthanide ion; (2) the variation of the intercept of the low-slope straight lines describing the dependence of $q^0_{\mathrm{s.l.}}/q_{\mathrm{s.l.}}$ on the concentration of the quenching agent (trans-stilbene) with increased ratio of the concentrations of Eu^{3+} and the ketone (Fig. 6); (3) the decrease of $q_{\mathrm{s.l.}}$ following the introduction into the solution of salts of gadolinium(III), which does not quench triplet states but is capable of forming stable complexes with the ketone and competing in this respect with Eu^{3+} ions. The presence of gadolinium ions hardly influences the slope of the two straight lines which describe approximately the variation of $q^0_{\mathrm{s.l.}}/q_{\mathrm{s.l.}}$ with the concentration of *trans*-stilbene.

The validity of the assumption made in the derivation of Eqns. (12)–(16) that one can neglect the dissociation of complexes of the type $[^3\mathrm{K{-}Ln}^{3+}]$, i.e. that $\omega_{\mathrm{t}} + \omega_{\mathrm{phch}} \gg k'_{\mathrm{dis}}$, where k'_{dis} is the rate constant for the dissociation of the complex, is confirmed by the weak influence of a change of temperature on the slope of the low-slope straight line in Fig. 7.

A study was made of the influence of electron-donating and electron-accepting substituents in ketones on the rate constants of the intramolecular and intermolecular energy transfer to lanthanide ions. The values of k_{t} and ω_{t} are listed in Tables 10 and 11. ω_{t} increases when electron-donating groups ($\mathrm{OCH_3}$, $\mathrm{OC_2H_5}$)¶ are introduced into the benzene rings of benzophenone and falls when electron-accepting groups (Br, Cl) are introduced. Substituents have a similar effect also on k_{t}, but the amplitude of the relative changed in k_{t} is smaller under these conditions. It has also been shown that k_{t} and ω_{t} increase with decrease of the electron-donating capacity of the solvent (see Table 11). Unfortunately the solvents employed in the investigation contain an admixture of water, which naturally complicated the observed picture. The admixture of water has a particularly marked influence in the study of energy transfer in solvents which are weak electron donors.

Valuable information was obtained from the study of the temperature dependence of k_{t}. This phenomenon was investigated in greatest detail in acetone and acetonitrile for 4-ethoxy-4′-methoxybenzophenone and 4-methoxybenzophenone as the energy donors and Eu^{3+} as the energy

Table 11. Intermolecular (k_{t}, litre $\mathrm{mole}^{-1}\mathrm{s}^{-1}$) and intramolecular ($\omega_{\mathrm{t}}$, s^{-1}) rate constants for energy transfer from the triplet molecules of aromatic ketones to Eu^{3+} ions in various solvents. Estimation of the activation energies for the transfer process (ΔE, kcal mole^{-1}) and the stability constants of the $[^1\mathrm{K{-}Eu}^{3+}]$ complexes (β_1, litre mole^{-1}) at 293 K (according to the data of Sveshnikova et al.[77]).

Energy donor	Methanol $DN \sim 20$; $\varepsilon = 32.6$			Acetone (moist) $DN = 17$; $\varepsilon = 20.7$				Acetonitrile (moist) $DN = 14$; $\varepsilon = 37.5$				Acetic anhydride $DN = 10$; $\varepsilon = 20.7$			
	$10^{-7}\cdot k_{\mathrm{t}}$	ΔE	β_1	$10^{-7}\cdot k_{\mathrm{t}}$	ΔE	$10^{-7}\cdot\omega_{\mathrm{t}}$	β_1	$10^{-7}\cdot k_{\mathrm{t}}$	ΔE	$10^{-7}\cdot\omega_{\mathrm{t}}$	β_1	$10^{-7}\cdot k_{\mathrm{t}}$	ΔE	$10^{-7}\cdot\omega_{\mathrm{t}}$	β_1
4-Ethoxy-4′-methoxybenzophenone	5.5	3.0	<0.2	13	3.2	250	~ 5	nc.	—	600	>50	nc.	—	350	>50
4-Methoxybenzophenone	3.0	3.2	<0.2	7	2.2	40	~ 0.6	24	2.3	120	~ 5	—	—	—	—
Acetophenone	5.0	—	<0.2	20	2.0	nc*	<0.2	—	—	—	—	37	—	34	~ 5
4-Bromobenzophenone	1.3	—	<0.2	3.4	1.8	nc.	<0.2	14	—	8	~ 1.4	—	—	—	—
4,4′-Dichlorobenzophenone	—	—	—	1.3	1.4	nc.	<0.2	4.6	1.2	3	~ 0.4	—	—	—	—

*nc = no complex.

¶ Stable lanthanide complexes with stronger electron donors—aromatic acid anions ($\mathrm{Ar{-}COO^-}$)[84] and alkoxyacetophenones[85]—are also observed in solvents characterised by a higher donor number (methanol)[84].

acceptor. With increase of temperature, k_t rises exponentially and the calculated activation energies for the formation of a complex of the triplet ketone and Eu^{3+} are 1–3 kcal $mole^{-1}$ (Table 11).

Presumably the rate constant k_t for the diffusional energy transfer between the triplet ketone and the lanthanide ion is described by the following expression:

$$k_t = A e^{-\frac{\Delta E}{kT}},$$

where the coefficient A is proportional to the number of encounters between the triplet ketone molecules and the lanthanide ions, i.e. to k_d, and to the duration of each encounter Δt_{enc}, i.e. $A = k_d \Delta t_{enc}$. Since Δt_{enc} is inversely proportional to k_d, A will not vary as k_d increases and can therefore be regarded as independent of temperature. The second factor characterises the probability of the incorporation of the triplet ketone in the first coordination sphere of the lanthanide ion during the encounter. It increases exponentially with increase of temperature. The values of ΔE obtained diminish with decrease of the electron-donating capacity of the ketone. This may be due to the change in the bonding energy between the ketone and the water molecules present in solution. Experiments on energy transfer uncomplicated by the presence of an admixture of water are extremely desirable.

Thus experiment showed that the rate constant for the intermolecular energy transfer from aromatic ketones to lanthanide ions in solution is determined by the chemical incorporation of the triplet ketone molecule in the first coordination sphere of the lanthanide ion and not by the physical energy transfer process. The rate of such incorporation depends on the chemical properties of the triplet state of the ketone. It is much higher for triplet ketones with the lowest level of the n,π^* type compared with ketones in which this level is of the π,π^* type, and increases following the introduction of electron-donating substituents into the benzene rings of the ketones (Table 10).

The study of the dependence of the rate constant for the intermolecular energy transfer from aromatic ketones with n,π^* and π,π^* triplet levels on the atomic number of the lanthanide ion, undertaken in a number of investigations[74-77], showed that, despite the considerable differences between the absolute values of k_t for transfer from the n,π^* and π,π^* levels, the relative changes in k_t in the series of lanthanide ions take place approximately in parallel (see Fig. 8). We believe this to be an additional confirmation of the hypothesis that k_t is mainly determined by the rate of incorporation of the triplet ketone in the first coordination sphere of the lanthanide ion and that this rate varies appreciably in the series of lanthanides.

The values of k_t cannot be unambiguously related to the rate of incorporation in the complex only for very low values of ω_t, which are observed for a highly endothermic energy transfer (to Gd^{3+} for ketones with the $^3\Gamma$ state of the n,π^* type and to Gd^{3+}, Dy^{3+}, Tb^{3+}, etc. for ketones with the $^3\Gamma$ state of the π,π^* type), since in the energy transfer method the indicator is the subsequent quenching of the triplet in the complex. In the interaction with Gd^{3+} and other ions, this quenching cannot occur for energetic reasons and there may be sufficient time for the dissociation of the complex $[^3K\text{–}Gd^{3+}]$.

With increase of temperature, there is also an increase of the relative concentration of stable ketone–lanthanide ion complexes in the ground state in acetone and acetonitrile. This is consistent with Matovich and Suzuki's observation[58] that the temperature dependence of the energy transfer reaction is characteristic of an endothermic process. We believe that the observed type of temperature dependence of the concentration of complexes of the type $[^1K\text{–}Ln^{3+}]$ in acetone and acetonitrile is associated with the competition between various ligands in the first coordination sphere of the lanthanide ion, in particular with the competition between the aromatic ketone and the dissolved water as a ligand.

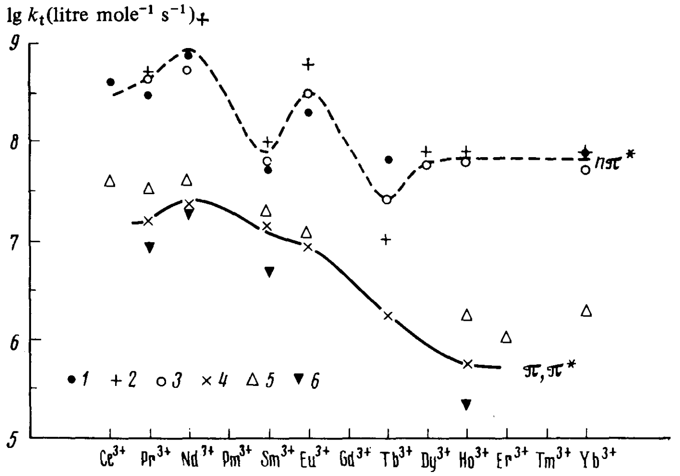

Figure 8. Dependence of the logarithms of the rate constants for energy transfer from aromatic ketones in the triplet state to lanthanide ions on the atomic number of the latter in moist acetone at 293 K: 1) acetophenone; 2) benzophenone; 3) benzoylpyridine; 4) 4-phenylbenzophenone; 5) methyl 2-naphthyl ketone; 6) 9-anthryl methyl ketone. For ketones with the lowest $^3\Gamma$ state of the n,π^* type, the values of k_t were measured by the method of competing lanthanide ions with energy transfer to Eu^{3+}; for ketones with the $^3\Gamma$ state of the π,π^* type, the flash photoexcitation method was used.

2. Energy Transfer from Lanthanide Ions to Organic Molecules with Excitation of the Triplet Level

Vavilov and Sevchenko[86] did not observe a decrease of the luminescence yield of an alcoholic solution of Sm^{3+} in the presence of typical fluorescence quenching agents: aniline, nitrobenzene, resorcinol, KI, etc. However, recently Aleksandrov et al.[87] and Kleinerman[88] noted a decrease in the decay time and in the intensity of the Eu^{3+} luminescence in solution after the addition of aromatic hydrocarbons, whose triplet level lies below the resonance level ($^5D_0$) of the Eu^{3+} ion. Subsequently Ermolaev and Tachin[40,48,49,81,89,92] made a detailed study of this phenomenon and showed that it is due to the non-radiative energy transfer from the lanthanide ions (Tb^{3+}, Eu^{3+}, and Dy^{3+}) to the organic molecules with excitation of the latter to the triplet state. The energy transfer takes place via the exchange resonance mechanism. The luminescence of the

Eu^{3+} ($^5D_0$) ion, which exhibits the maximum electron affinity, is quenched in some cases also via the electron transfer mechanism[89]. Thus two processes are responsible for the quenching:

$$^{m}(Ln^{3+})^{*} + {}^{1}A \rightarrow {}^{n}(Ln^{3+}) + {}^{3}A, \tag{18}$$

$$^{m}(Ln^{3+})^{*} + {}^{1}A \rightarrow {}^{k}(Ln^{2+}) + {}^{2}A^{\dot{+}} \ . \tag{19}$$

The electron energy level diagram for reaction (18) is illustrated in Fig. 9. The energy transfer process is not accompanied by the internal conversion of some of the electronic excitation quanta. This was demonstrated by Tachin and Ermolaev[90], who investigated the energy transfer from $Tb^{3+}(^5D_4)$ to Eu^{3+} in acetone via methyl 2-naphthyl ketone as an intermediate and showed that one excited Eu^{3+} ion corresponds to one quenched Tb^{3+} ion.

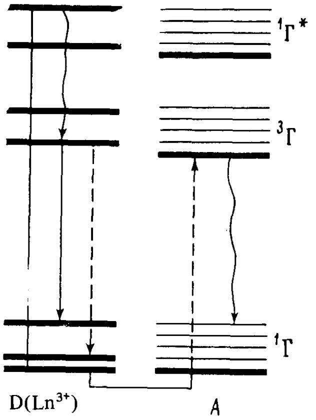

Figure 9. Schematic illustration of the electronic levels in the energy transfer from lanthanide ions to organic molecules with excitation of the latter to the triplet state.

Table 12 lists the values of[89] k_t (in moist acetone) for energy transfer from lanthanide ions to various aromatic molecules. It shows that (1) k_t is much lower than the diffusion rate constant and (2) the k_t for transfer to molecules with substituents ($-COCH_3$, $\rangle$N, etc.) capable of forming coordinate bonds with lanthanide ions are higher by 1–2 orders of magnitude than for energy transfer to molecules of unsubstituted aromatic hydrocarbons. The k_t for energy transfer to aromatic ketones are close to the corresponding values for energy transfer from aromatic ketones ($^3\pi,\pi^*$) to lanthanide ions (cf. Tables 10 and 12 and Fig. 8), provided that the reaction is exothermic in both cases. The closeness of the observed values of k_t demonstrates the complexity of the kinetics of these processes. Presumably the rate-limiting step of the energy transfer from lanthanide ions to aromatic ketones as well as that in the reverse transfer is the incorporation of the aromatic ketone in the first coordination sphere of the lanthanide ion. The difference is that, in the energy transfer from the lanthanide ion, the aromatic ketone in the ground singlet state is incorporated in the hydration shell of the excited lanthanide ion, while in the energy transfer from the triplet ketone the latter is incorporated in the inner solvation shell of the non-excited lanthanide ion. The experimental values of k_t for both types of transfer do not differ greatly, in agreement with the weak influence of the excitation of the shielded $4f$ shells on the chemical properties of lanthanide ions and also with the insignificant changes in the electron-donating properties of aromatic ketones on excitation to the π,π^* triplet state relative to the ground state[91].

Table 12. The rate constants for energy transfer from lanthanide ions to organic molecules with transition of the latter to the triplet state in moist acetone [$k_d = 2.1 \times 10^{10}$ litre $mole^{-1}s^{-1}$; in air; 293 K (data of Ermolaev and Tachin[89]); E_A = energy of the $^3\Gamma$ state of the energy acceptor].

Quenching agent	E_A, cm^{-1}	k_t^*, litre $mole^{-1}$ s^{-1}
Eu^{3+} donor (energy of $^5D_0$ emission level 17 200 cm^{-1})		
1-Anthryl methyl ketone	15 160	$4.7 \cdot 10^6$
Acridine	15 840	$1.2 \cdot 10^6$
Anthracene	14 900	$1.0 \cdot 10^5$***
Methyl 2-naphthyl ketone	20 800	$1.0 \cdot 10^3$
NN-Dimethylaniline	26 600	$5.3 \cdot 10^5$**
Tb^{3+} donor (energy of $^5D_4$ emission level 20 500 cm^{-1}		
Methyl 2-naphthyl ketone	20 800	$2.1 \cdot 10^6$
Acridine	15 840	$1.6 \cdot 10^6$
Fluorenone	19 200	$1.0 \cdot 10^6$
1-Naphthoic acid	20 200	$8.5 \cdot 10^5$
Anthracene	14 900	$1.0 \cdot 10^5$
Dy^{3+} donor (energy of $^4F_{9/2}$ emission level 20 800 cm^{-1})		
Fluorenone	19 200	$8.9 \cdot 10^5$
Methyl 2-naphthyl ketone	20 800	$7.6 \cdot 10^5$

* Accuracy of the measurements of $k_t \sim 20–30\%$.

** Quenching via the electron transfer mechanism.

*** An error was made in the study of Ermolaev and Tachin[89]. The corrected value is quoted here.

Ermolaev and Tachin[92] made a comparative study of the influence of temperature and the solvent on k_t for energy transfer from Tb^{3+} to 9-anthryl methyl ketone (AMK) and to anthracene (A). The results obtained are listed in Table 13, showing that k_t for the transfer from Tb^{3+} to the ketone decreases by more than 2 orders of magnitude with increase of the electron-donating capacity of the solvent molecules, while k_t for the transfer to anthracene depends little on the electron-donating capacity of the solvent. A significant difference between these two examples is also observed in the temperature variation of k_t. In the first case, involving energy transfer to the ketone, the process has an activation energy which increases with the increase of the donor number of the solvent and decreases to zero for solvents with a high electron-donating capacity. On the other hand, k_t for energy transfer to anthracene is independent of temperature, except in dimethyl sulphoxide. In solvents with a high electron-donating capacity, the values of k_t for energy transfer to 9-anthryl methyl ketone and anthracene agree within the limits of experimental error. Evidently the anthracene molecule cannot penetrate the first coordination sphere of the lanthanide ion and k_t corresponds in this case to energy transfer to the acceptor molecule in the second coordination sphere. Similarly the 9-anthryl methyl ketone molecule likewise does not penetrate the first coordination sphere in solvents with a high electron-donating capacity. The relatively high rate constant for energy transfer to the ketone in solvents with a low electron-donating capacity (which is at least 3 orders of magnitude lower than the diffusion-limited rate constant) undoubtedly corresponds to the incorporation of the ketone in the first coordination sphere of the excited Tb^{3+} ion.

Table 13. The rate constants for energy transfer (k_t) from Tb^{3+} ($^5D_0$ = 20 500 cm^{-1}) to 9-anthryl methyl ketone (AMK) ($^3\Gamma$ = 15 160 cm^{-1}) and anthracene (A) ($^3\Gamma$ = 14 900 cm^{-1}) in liquid dried solutions at 293 K. The estimated rates of incorporation of AMK in the first coordination sphere of Tb^{3+} [$k_{inc} = k_t(AMK) - k_t(A)$] and the activation energies for this reaction (ΔE_{inc}).

Solvent	DN, kcal $mole^{-1}$	τ_0, ms	Acceptor			k_{inc}, litre $mole^{-1}$ s^{-1}	ΔE_{inc}, kcal $mole^{-1}$
			9-anthryl methyl ketone	Anthracene			
			k_t, litre $mole^{-1}$ s^{-1}	k_t, litre $mole^{-1}$ s^{-1}	ΔE, kcal $mole^{-1}$		
Acetonitrile	14.1	1.7	$1.0 \cdot 10^7$	$1.4 \cdot 10^5$	0	$1.0 \cdot 10^7$	3.0
Acetone	17.0	1.7	$3.4 \cdot 10^6$	$1.8 \cdot 10^5$	0	$3.3 \cdot 10^6$	3.2
			$4.0 \cdot 10^5$*	$1.9 \cdot 10^5$	—	—	—
Ethyl acetate	17.1	1.8	$1.9 \cdot 10^6$	—	—	—	4.1*
Propanol	—	1.35	$3.2 \cdot 10^5$	$9.5 \cdot 10^4$	0	$2.0 \cdot 10^5$	4.8
Methanol	—	1.35	$2.1 \cdot 10^5$	$1.1 \cdot 10^5$	0	$1.0 \cdot 10^5$	5.0
Pyridine	33.1	1.3	$1.9 \cdot 10^5$	$1.1 \cdot 10^5$	0	$8.0 \cdot 10^4$	5.5
Trimethyl phosphate	23.0	2.7	$3.2 \cdot 10^4$	$3.2 \cdot 10^4$	0	$<10^3$	—
Tributyl phosphate	23.7	2 4	$4.2 \cdot 10^4$	$4.2 \cdot 10^4$	0	$<10^3$	—
			$(4.2 \cdot 10^4)$ *	$(4.2 \cdot 10^4)$ *	0	—	—
Dimethyl sulphoxide	28.9	2 6	$7.2 \cdot 10^4$	$7.2 \cdot 10^4$	2.0***	$<10^3$	—

* Moist solution.

** Activation energy $\Delta E[k_t(AMK)]$.

*** Activation energy $\Delta E[k_t(AMK)] = \Delta E[k_t(A)]$.

The observed activation energies ΔE were calculated from the variation of $\ln [k_t(AMK) - k_t(A)]$ with the reciprocal of temperature and probably correspond to the activation energy for the dissociation of the solvent molecule from the first coordination sphere of the lanthanide ion. The last column of Table 13 lists the rates of incorporation of the ketone in the first coordination sphere of the Tb^{3+} ion in the $^5D_4$ state, calculated from the formula $k_{inc} = k_t(AMK) - k_t(A)$. In dimethyl sulphoxide, there is probably an ordered arrangement of the molecules in the second coordination sphere and the activation energy for incorporation in the second coordination sphere is observed.

We believe that the findings described above demonstrate quite convincingly the considerable scope of the energy transfer method in the study of reversible and dynamic complex formation reactions between organic molecules and lanthanide ions in solution. The following observations have been made with the aid of this method: (1) a new type of ion pairs comprising anionic dyes and lanthanide ions in solutions has been discovered; (2) equilibrium in solvents with a low electron-donating capacity between aromatic ketone–lanthanide ion complexes and solvated ketones and lanthanide ions has been demonstrated and the stability constants of the complexes have been estimated; (3) a number of conclusions have been drawn concerning the dynamics of the incorporation of triplet ketones in the inner coordination sphere of non-excited lanthanide ions and the activation energies for this process have been determined; (4) information has been obtained about the incorporation of a non-excited aromatic ketone in the inner solvation shells of excited lanthanide ions and the activation energies for this process in various solvents have been determined.

The experimental technique of studies on complex formation by the energy transfer method is in the main simple and does not require expensive apparatus. In most cases, it comprises the usual photoelectric apparatus for the measurement of the intensity and rate of decay of luminescence. Such apparatus and the required techniques have been described in a recently published translation of Parker's book[93]. More complex flash photoexcitation methods have been described by Shakhverdov[94] and Boag[95] and in the monograph by Calvert and Pitts[96], and laser photoexcitation methods are given in the paper by Porter and Topp[97]. We are certain that the energy transfer method will soon become the normal procedure in chemical laboratories dealing with problems of coordination chemistry.

ADDED IN PROOF

During the preparation of the review for the press, a detailed survey of the processes involving the sensitisation and quenching of the luminescence of coordination compounds (mainly those of transition metal ions) was published by Balzani et al.[98] Their survey and our reviews in this journal complement one another successfully.

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Silicon Analogues of Carbenes

E.A.Chernyshev, N.G.Komalenkova, and S.A.Bashkirova

A systematic account is given of data published up to 1975 on the preparation and chemical properties of silicon analogues of carbenes—short-lived bivalent silicon compounds (silylenes). Methods for their formation with the aid of high temperatures as well as other sources of energy (silent electric discharge, photolysis, and radiolysis) are discussed.

The chemical properties of silylenes have been classified in accordance with three types: (1) polymerisation; (2) insertion in single bonds; (3) addition to multiple bonds.

The possibility of employing silylenes (particularly dichlorosilylene) for preparative purposes is discussed. Attention has been concentrated on experimental data relevant to the gas-phase reactions of silylenes.

The bibliography includes 299 references.

CONTENTS

I. INTRODUCTION

The chemistry of bivalent Group IVB elements has been attracting much attention in recent years. The interest aroused by these substances is due to the considerable advances in the theoretical and practical developments of the chemistry of carbenes, which already have a twenty year old history. However, the chemistry of organic derivatives of the elements which are carbene analogues, particularly the chemistry of silylenes, has not so far passed beyond the limits of laboratory tests owing to the complete absence of convenient methods for their synthesis.

Since the publication of the first reviews[1,2] devoted to the most important aspects of the chemistry of silylenes, the number of studies in this field has greatly increased and continues to increase. This is due to the advances in experimental techniques in the last decade—the development of methods for the creation of high temperatures and a high vacuum and also a new technique involving the quenching of the reaction mixture[3], which makes it possible to carry out the reactions of silylenes with a series of reactive organic compounds. Extensive experimental data have now accumulated on the chemistry of inorganic silylenes at low temperatures (−196°C) (the low-temperature condensation method), which has been surveyed in a number of reviews[5-8]; the similarity of the chemical properties of silicon monoxide, which is also of interest for syntheses at low temperatures[9], and those of other silylenes, for example difluorosilylene[7], has been noted. On the other hand, the gas-phase reactions of silylenes have not been described systematically (with the exception of the paper by Schaschel et al.[9]). Interesting communications have been published in which the stabilisation of silylenes by coordination in transition metal complexes is discussed[10-13]. Considerable advances have been made also in research on the physical properties of silylenes[14]. Methods for the generation of bivalent silicon compounds in extremely short time intervals (a millisecond or less), such as flash photolysis, electrical discharge, radioactive nuclear decomposition processes etc., have become common and make it possible not only to detect the presence of unstable species but also to determine their characteristics[15]. The development of methods for the matrix isolation[16-18] of such species greatly supplemented the available information about their nature and properties.

Apart from the purely theoretical interest in silylenes, attempts have been made in recent years to find direct practical applications for such species. From this standpoint, dihalogenosilicon derivatives are particularly promising[19]. Studies demonstrating the great synthetic possibilities of the employment of dichlorosilylene in gas-phase reactions have been published only in the last 3–4 years. Apart from a brief assessment of the present state of chemistry of silylenes, attention is concentrated in the present review of their "high-temperature" gas-phase chemistry, particularly that of dichlorosilylene, and the synthetic aspects of their utilisation.

II. METHODS OF SYNTHESIS

1. METHODS OF SYNTHESIS USING HIGH TEMPERATURES

The commonest methods for the preparation of bivalent silicon compounds involve high-temperature processes. Since pyrolytic methods for the preparation of inorganic and organic silylenes differ somewhat, we believe it to be useful to consider them separately.

A. Inorganic Silylenes

Short-lived silylenes can be isolated in high-temperature processes[3] only when the rate of cooling of these species is much higher than the rate of side reactions. Under the conditions of a high vacuum, it is possible to remove the gaseous species from the hot zone virtually without collisions and then condense them, which enables them to react with one another or with other condensed molecules. The high-temperature processes involving the formation of inorganic silylenes can be divided into processes at atmospheric pressure (1 atm) and low pressure (below 1 mmHg). We shall henceforth adhere to this classification.

1. Processes at atmospheric pressure. High-temperature processes at atmospheric pressure scarcely allow the isolation of silylenes, but they do make it possible to investigate their reactions and to carry out kinetic and thermodynamic studies. The reaction mechanism is then clear only in rare instances and in order to

account for the observed effects it is usually necessary to postulate the intermediate formation of silylenes on the basis of the determination of the composition of the mixture of final products.

Among processes of this type, involving the formation of inorganic silylenes, the reduction of tetrahalogenosilanes by silicon has been known for a long time[20,21]:

$$SiX_4(gas) + Si(solid) \overset{1000-1300°\,C}{\rightleftarrows} 2\ddot{Si}X_2(gas). \qquad (1)$$

The reviews[1,2] do not make it clear how the efficiency of reaction (1) depends on the nature of the halogen in the SiX_4 series, where X = F, Cl, Br, or I. A detailed study has now been made of the case where X = Cl.[22-35] The formation of $\ddot{Si}Cl_2$ has been confirmed by thermodynamic calculations[23,24,26,29-31] and kinetic studies[28]. However, it has been suggested recently that the composition of the gas phase is more complex and that considerable amounts of $\cdot\ddot{Si}Cl$ and $\dot{Si}Cl_3$ are present together with $SiCl_4$ and $\ddot{Si}Cl_2$.[36,37]

Reaction (1) for X = Br has also been investigated in detail[27,31,39] and that for X = I in less detail[27,31,38]. It is is noteworthy that di-iodosilylene can be obtained by this method, since both this species and silicon tetraiodide are appreciably dissociated into silicon and atomic iodine already at temperatures between 900° and 1000°C.[31,39] When X = F, the product is a mixture of gaseous, liquid, and solid subfluorides the composition of which has not yet been established exactly[20,40,41].

The reaction where X = Cl, Br, and I can serve as a source of pure silicon, which is used to coat surfaces with silicon[25,27,32,33,42,43]. In its preparative aspects, it has been used for the synthesis of trichlorosilane[34,44], mixed halogenosilanes[35], and chloromethylsilane[35]. In the absence of acceptors of dihalogenosilylenes, various compounds are formed as a function of reaction conditions—polymers $(-SiX_2-)_n$, linear polysilanes (Si_nCl_{2n+2}),[44] or cyclic polysilanes (Si_nCl_{2n}),[35] but a detailed structural study has not been made. On heating, the polymers are converted into perhalogenosilanes, starting from SiX_4 and extending as far as Si_6X_{14}; the residual subhalides have a molecular weight of approximately 1600.[35,44] It is probable that this entails also the formation of dihalogenosilylenes, the interaction of which with silicon tetrahalides actually leads to the formation of all the perhalogenosilanes.

The intermediate formation of dichlorosilylene also occurs in the reduction of silicon tetrachloride[45-51] or trichlorosilane[49,50,52,53] by hydrogen:

$$SiCl_4 + H_2 \xrightarrow{1000-2000K} \ddot{Si}Cl_2 + 2HCl \quad . \qquad (2)$$

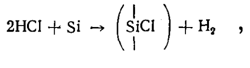
This reaction is widely used as a method for the preparation of pure silicon film coatings[48,49,51,52]. The formation and the important role of dichlorosilylene in these processes have been confirmed by thermodynamic calculations alone. There is no clear-cut information about other evidence or about the use of $\ddot{Si}Cl_2$, formed in this reaction, for synthetic purposes.

The possibility of employing trichlorosilylene in the "direct" synthesis of organochlorosilanes (250–400°C) when organic chlorides interact with silicon has been frequently discussed[54,55]. Andrianov and Golubtsov[56] have shown that it is generated by the reduction of copper(I) chloride by silicon:

$$2CuCl + Si \rightarrow 2Cu + \ddot{Si}Cl_2 \quad . \qquad (3)$$

Numerous facts confirming this view have now been observed[56,57]. Reliable evidence for the formation of dichlorosilylene in the "direct" synthesis was secured by the mass-spectrometric study of reaction (3).[58-60]

The information available previously[57,61,62] about the formation of dichlorosilylene in the "direct" synthesis of trichlorosilane,



$$2HCl + Si \rightarrow \left(\overset{|}{\underset{|}{Si}}Cl\right) + H_2 \quad , \qquad (4)$$

may be supplemented by the following remarks: mass-spectrometric data for the products desorbed from the surface of silicon before and after reaction (4) with the aid of a desorbing gas confirm the probability of the formation on the surface of the $\ddot{Si}Cl_2$ species which is capable of both desorption and of reaction with hydrogen chloride[63,64].

Various chlorosilanes can serve as convenient sources of inorganic silylenes in many instances. Thus is has been established recently that dichlorosilylene plays an important role in many pyrolytic processes occurring with participation of chlorosilanes[65-71].

It has been suggested in a paper by Sirtl and Reuschel[49] and then in a review[2] that the pyrolysis of trichlorosilane proceeds via the following mechanism:

$$HSiCl_3 \xrightarrow{>1100°} HCl + \ddot{Si}Cl_2 \quad . \qquad (5)$$

On the other hand, a detailed study of the products of its pyrolysis showed that, in the temperature range 500–750°C, hydrogen chloride is not formed in appreciable amounts[72]. A reinvestigation of the kinetics of the thermal decomposition of trichlorosilane confirmed these results[73]. It has now been established that the main products of the decomposition of $HSiCl_3$ are silicon tetrachloride, hydrogen, and silicon[72-74]. This suggests the following more probable general mechanism of its pyrolysis with formation of $\ddot{Si}Cl_2$:[67,68]

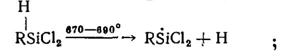
$$2HSiCl_3 \xrightarrow{650-670°} SiCl_4 + H_2 + \ddot{Si}Cl_2 \quad . \qquad (6)$$

Maksimova's categorical statement[69] that the pyrolysis of trichlorosilane proceeds via the radical mechanism

$$HSiCl_3 \rightleftarrows H + \dot{Si}Cl_3 \qquad (7)$$

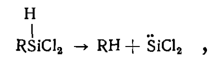
at 600°C and via mechanism (5) at 650°C is therefore puzzling. In this case, it is obviously more correct to postulate the dominant role of one of the two reactions, (6) or (7), in a particular temperature range.

It has been established that, apart from trichlorosilane, certain other organochlorosilanes can also serve as donors of dichlorosilylene and it is of interest that pyrolysis can proceed via two pathways[70]:



$$R\overset{H}{\overset{|}{Si}}Cl_2 \xrightarrow{670-690°} R\dot{Si}Cl_2 + H \quad ; \qquad (8)$$

$$2R\dot{Si}Cl_2 \longrightarrow RSiCl_3 + R\ddot{Si}Cl \quad ; \qquad (9)$$



$$R\overset{H}{\overset{|}{Si}}Cl_2 \rightarrow RH + \ddot{Si}Cl_2 \quad , \qquad (10)$$

where R = α-$C_{10}H_7$, C_6H_5, or CH_3.

Mechanism (10) is satisfactorily confirmed by the formation of the corresponding amounts of naphthalene, benzene, and methane. It is noteworthy that, with increase of the temperature of the reaction zone from 640° to 690°C, pyrolysis proceeds via mechanism (10) to a greater extent. A similar pyrolysis mechanism [reaction (9) and (10)] has been proposed for methylsilane[75]:

$$CH_3SiH_3 \rightleftarrows CH_2\ddot{Si}H + H_2 \quad ; \qquad (11)$$

$$CH_3SiH_3 \rightleftarrows \ddot{Si}H_2 + CH_4 \quad . \qquad (12)$$

According to other data[76], the decomposition of methylsilane is not accompanied by the formation of $\ddot{Si}H_2$.

Methane has not been detected among the reaction products in the study by Ring et al.[77] Evidently, more detailed studies are required in order to refine the mechanism of the pyrolysis of methylsilane. However, the simultaneous occurrence of a reaction with formation of a silyl radical [reactions of type (7) or (8)] has been noted in all cases. The radical reactions greatly complicate the pyrolytic processes involving silanes and constitute a significant disadvantage of the latter as silylene donors.

There are literature data showing that the intermediate formation of silylenes is observed also in the pyrolysis of tetrahalogenosilanes and silane:

$$\mathrm{SiX_4 \rightarrow \ddot{S}iX_2 + X_2}\ . \qquad (13)$$

Reaction (13) occurs when X = Cl [24] or I [39] at 900°C and when X = H [78,79] at 400°C.

Despite the fact that the pyrolysis of silane has been investigated in considerable depth for a long time[78], there is at present no unanimous view concerning the mechanism of the initial stage of its decomposition—some workers[78,79] suggest a mechanism involving the formation of silylene [reaction (13)], while others[77] propose a radical-chain mechanism:

$$\left.\begin{aligned} \mathrm{SiH_4} &\rightarrow \mathrm{\dot{S}iH_3 + H} \ ; \\ \mathrm{H + SiH_4} &\rightarrow \mathrm{H_2 + \dot{S}iH_3} \ ; \\ \mathrm{\dot{S}iH_3 + SiH_4} &\rightarrow \mathrm{Si_2H_6 + H} \ ; \\ \mathrm{2\dot{S}iH_3} &\rightarrow \mathrm{Si_2H_6}\ . \end{aligned}\right. \qquad (14)$$

The arguments in support of both points of view depend only on the reliability of the thermochemical information; however, it has been correctly pointed out[79] that the scatter of the available $H-SiH_3$ and $H_3Si-SiH_3$ bond dissociation energies is much greater than the expected differences between the activation energies for reactions (13) and (14). The contradictory nature of the available data on this problem so far precludes a definite conclusion. However, the latest calculations of the absolute entropies of formation of silylene and the silyl radical suggest that preference should be given to reaction (13).[80]

An effective method for the generation of inorganic silylenes proved to be the thermal decomposition of polysilanes and their halogeno-derivatives. The decomposition of hexahalogenodisilanes, which was observed by Friedl and Ladenburg[81] as early as 1880, has not received due attention until the present time:

$$x\mathrm{Si_2X_6} \rightarrow x\mathrm{SiX_4} + (\mathrm{SiX_3})x, \qquad (15)$$

where X = I,[81-83] Cl,[83] or Br.[83]

The hypothesis of the intermediate formation of dihalogenosilylenes in reaction (15) was put forward about 10 years ago[84] and has been frequently quoted[2,76,85], but its mechanism still remains obscure. It was believed previously that hexachlorodisilane is capable of decomposing on pyrolysis via a homolytic mechanism and the formation of dichlorosilylene was explained by the recombination of two trichlorosilyl radicals[84,86]:

$$\mathrm{Cl_3SiSiCl_3 \xrightarrow{\Delta} 2\dot{S}iCl_3}\ ; \qquad (16)$$

$$\mathrm{\dot{S}iCl_3 + \dot{S}iCl_3 \rightarrow \ddot{S}iCl_2 + SiCl_4}\ . \qquad (17)$$

An interesting attempt to predict the direction of pyrolysis of disilanes[76], including hexachlorodisilane, was made very recently and it has been suggested that the thermal dissociation of hexachlorodisilane has a carbenoid mechanism:

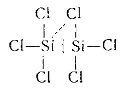
$$\mathrm{Cl_3SiSiCl_3 \rightarrow \ddot{S}iCl_2 + SiCl_4}\ . \qquad (18)$$

The study of the kinetics of the thermal decomposition of hexachlorodisilane under flow conditions in a quartz reactor in the temperature range 360–420°C established that its decomposition is described satisfactorily by the equation for first-order kinetics with $E_a = 49.6 \pm 1.2$ kcal mole^{-1} and lg$A$ (s^{-1}) = 13.8 ± 0.36. The heats of reactions (16) and (18) are respectively 77 ± 5 and 48 ± 5 kcal mole^{-1}.[87] Using these data, it is possible to show approximately that the preferential occurrence of reaction (18) requires that the activation energy for the reverse reaction

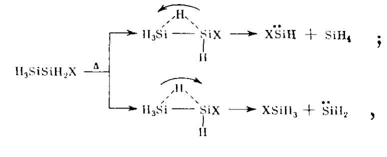
$$\mathrm{\ddot{S}iCl_2 + SiCl_4 \rightarrow Si_2Cl_6} \qquad (19)$$

should not exceed 27–28 kcal mole^{-1}. Although its value has not been determined, it is known that reaction (19) takes place rapidly both in the gas phase and on cocondensation, so that one can assume with a good deal of certainty that reaction (18) is a primary process in the decomposition of hexachlorodisilane.

This is confirmed directly by the results obtained recently in a spectroscopic study of the primary products of the pyrolysis of hexachlorodisilane by the matrix isolation method[88]. The dissociation of Si_2Cl_6 under the conditions described takes place at temperatures in the range 600–650°C. The reaction products are only silicon tetrachloride and dichlorosilylene. These results permit the final conclusion that the pyrolysis of hexachlorodisilane (as well as higher perchloropolysilanes)[89-91] is an example of the α-elimination reaction and involves attack by the chlorine atom linked to one of the silicon atoms on the neighbouring silicon atom with formation of "bridging" chlorine:



The pyrolysis reactions of higher silanes have been investigated comparatively recently and it has never been established reliably that disilane and many substituted disilanes are effective sources of silylene and substituted silylenes. The mode of decomposition of the compounds H_5Si_2X is represented by two pathways involving intramolecular 1,2-transfer of hydrogen:



(20)

(21)

where X = H,[93-97] Cl, F,[98] or CH_3.[99]

It is suggested on the basis of the latest kinetic investigations that the pyrolysis of trisilane likewise proceeds in two ways [Eqns. (20) and (21)] woth formation of silylene and silylsilylene ($H\ddot{S}iSiH_3$).[100]

Two similar decomposition pathways have been found for disubstituted disilanes, but the 1,2-transfer of the atom X was not observed:

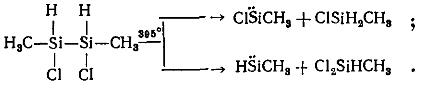
$$\mathrm{1,1\text{-}X_2Si_2H_4 \rightarrow \ddot{S}iH_2 + X_2SiH_2}\ ; \qquad (22)$$

$$\mathrm{1,1\text{-}X_2Si_2H_4 \rightleftarrows \ddot{S}iX_2 + SiH_4}\ , \qquad (23)$$

where X = Cl [98] or CH_3.[99]

Reaction (23) is less favourable for dihalogenodisilanes and reaction (22) only is observed for 1,1-difluorodisilane[98]

Interesting results have been obtained for the decomposition of *sym*-$Cl_2Si_2H_2(CH_3)_2$ [Eqns. (24) and (25)], suggesting that the 1,2-transfer of the Cl atom is nevertheless possible in those cases where the latter and the hydrogen atom are in identical environments[98]:



$$H_3C-\overset{H}{\underset{Cl}{Si}}-\overset{H}{\underset{Cl}{Si}}-CH_3 \xrightarrow{395°} Cl\ddot{Si}CH_3 + ClSiH_2CH_3 \quad ; \qquad (24)$$

$$\qquad\qquad\qquad \xrightarrow{395°} H\ddot{Si}CH_3 + Cl_2SiHCH_3 \quad . \qquad (25)$$

The ratio of the contributions of reactions (24) and (25) is 4:1.

2. Processes at a low pressure in the system. The study of such processes in the last 15 years has developed considerably, since they make it possible to obtain at a high temperature unstable and highly reactive gaseous atomic and molecular species. When the processes are carried out at a low pressure, one can reduce to a minimum the number of mutual collisions of the species and their collisions with the walls. Among the latest advances, particular mention should be made of certain processes involving the formation of inorganic silylenes *in vacuo*:

(a) evacuation of metals, for example:

$$Si(solid) \underset{}{\overset{1400°\,C,\ 10^{-5}\ mmHg}{\rightleftarrows}} \cdot\dot{\underset{\cdot}{Si}}\cdot\ (gas) \qquad (26)$$

followed by the insertion of the atoms in Si–X bond;

(b) reduction methods, for example:

$$Si(solid) + SiO_2(solid) \overset{1200°\,C,\ 10^{-3}\ mmHg}{\rightleftarrows} 2\ddot{Si}O\ (gas); \qquad (27)$$

$$Si(solid) + SiX_4(gas) \overset{115°\,C,\ 1\ mmHg}{\rightleftarrows} 2\ddot{Si}\,X_2\ \ (gas); \qquad (28)$$

(c) thermal decomposition of halogenosilanes.

Methods a and b presuppose the possibility of isolating the silylenes by condensation as a result of extensive cooling (down to –196°C) and also the investigation of their chemical properties by cocondensation with other compounds[3–6,9,101].

(a) Evaporation of silicon. In 1967 Skell and Owen published a study devoted to the chemistry of atomic silicon[102]. Almost simultaneously, another report was published about the high reactivity of atomic silicon[3]. Up to that time, only the molecular composition of silicon vapour had been described in the literature[103]. The above investigators[3,102] were able to isolate from the hot zone at a low pressure extremely reactive atoms, which can be obtained under the conditions of reaction (26), or on thermal evaporation of silicon[102,104], or by bombarding silicon with electrons[5,101,104–106]. Under these conditions, the content of polymeric species in gaseous silicon is much smaller than in carbon vapour[107]; at a low pressure, the dominant species are silicon atoms[5].

(b) The reduction reactions. This method is most convenient for the preparation of a highly reactive silylene—silicon monoxide ($\ddot{Si}O$). Like silicon atoms, it can be isolated only at a very low pressure.

The formation of gaseous $\ddot{Si}O$ as an intermediate in the reduction of silicon dioxide has been known for a long time[108–118]. It has been found that reducing agents may be arranged in the following sequence in terms of decreasing activity[116,117]:

$$Si(gas) > C(solid) > Si(liq.) > Si(solid) > FeSi(liq.) > FeSi(solid) > SiC.$$

It has been reported that silicon monoxide is also formed in the reduction of silicon dioxide by hydrogen[119,121]. Silicon monoxide is likewise formed when silicon is treated with an oxidising agent[122,123] such as a metal oxide, for example by the reaction

$$2Si + Al_2O_3 \overset{1800°}{\rightleftarrows} Al_2O_3\,(gas) + 2\ddot{Si}O\ (gas) \qquad (29)$$

and also on heating silicon dioxide alone above 1600 K.[124–127] However, the best preparative method is the reduction of pure SiO_2 (99.7%) by pure silicon (99.8%) via reaction (27).[9,118,125,127–129] It is of interest that gaseous silicon monoxide can be obtained for preparative purposes by heating "solid SiO" *in vacuo*[9,130,131], the content of the dimer being only 0.1% under these conditions.

Owing to the technical difficulty of maintaining a sufficiently low pressure in the high-temperature system, the gaseous $\ddot{Si}O$ molecule, which has been known for a long time, has not been used in further reactions until recently[9,130,131]. The formation of silicon monosulphide is also a reaction of the same type[132–134]:

$$SiS_2(solid) + Si(solid) \overset{900–1150°,\ <0.1,\ mmHg}{\rightleftarrows} 2\ddot{Si}S\ (gas). \qquad (30)$$

It is much easier to synthesise and isolate dihalogenosilylenes under the conditions described[3]. All the dihalogenosilylenes have been obtained under the conditions of reaction (28), but $\ddot{Si}Br_2$,[135–137] $\ddot{Si}I_2$,[136,138] and $\ddot{Si}Cl_2$,[136,139] are less stable than $\ddot{Si}F_2$.[136] It has been shown that di-iodosilylene cannot be synthesised efficiently by this procedure[138]. Its polymer has been obtained in approximately 1% yield at 800–900°C. The synthesis of difluorosilylene reported previously in fact also involved the formation of the polymer $(-SiF_2-)_n$.[136,140]

Since Timms devised recently a suitable apparatus[3,6,101], which provides for the rapid transfer of dihalogenosilylenes by suction into the region at a pressure of the order of 10^{-5} mmHg, it has been possible to avoid the gas-phase polymerisation of dichloro- and dibromo-silylenes, to prevent their reaction with the corresponding silicon tetrahalides, and hence to obtain them in high yields (95 and 80% respectively)[101,141–143]. Owing to its higher stability, difluorosilylene can be obtained in simpler apparatus than that of Timms[3,144] in fairly high yields (up to 65%) at a residual pressure of 0.1–0.2 mmHg.[145–147]

(c) Thermal decomposition of halogenosilanes. The thermal methods for the synthesis of inorganic silylenes *in vacuo* have not been developed quite so effectively as the analogous methods at atmospheric pressure (see above); nevertheless, it has been stated that the thermal decomposition of hexafluorodisilane[148] [reaction (15)] in a high vacuum is the best method for the generation of difluorosilylene. According to the authors, this procedure makes it possible to obtain $\ddot{Si}F_2$ completely free of oxygen.

The pyrolysis *in vacuo* of the tetrahalogenosilanes $SiBr_4$[149] and SiI_4,[138,149] which is treated merely as a method for the preparation of the polymers $(-SiX_2-)_x$, has been little studied. From the standpoint of the generation of silylenes on a preparative scale, these reactions evidently have no importance.

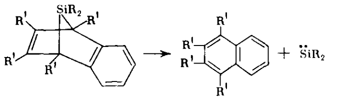
B. Organic Silylenes

Owing to the lack of a suitable method for the preparation of silylenes with organic substituents, these substances have been little studied until recently. There has been a considerable development of the chemistry of organosilylenes during the last ten years and there are now several methods for their synthesis.

1. Reduction of dialkyldichlorosilanes by metals. Analysis of studies of the reactions of dialkyldichlorosilanes with metals has shown that the available information about the possible formation of silylenes in this reaction is fairly contradictory. Skell and Goldstein[150,151] obtained convincing proof of the formation of dimethylsilylene when dichlorodimethylsilane reacts with potassium in the gas phase (t = 260–280°C), having trapped $\ddot{Si}(CH_3)_2$ by trimethylsilane.

However, the analogous formation of silylene in the condensed phase has not been established[152,153]. Despite the fact that the reaction of dichlorodimethylsilane with lithium[154] is also consistent with the hypothesis of the intermediate formation of $\ddot{Si}(CH_3)_2$,[2] convincing evidence for this has not been obtained so far. Since the yields of reaction products are very low (2–10%) when the above source of silylenes is used and more convenient methods for the generation of organic silylenes are available at the present time, the reaction of alkali metals with dialkyldichlorosilanes in solvents has not assumed practical importance in the investigation of silylenes.

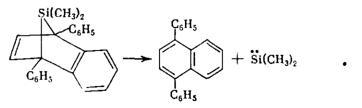
2. Thermolysis of 7-silanorbornadienes. This method, proposed in 1964 by Gilman et al.[155,156], is widely used for the preparative synthesis of dimethyl- and diphenyl-silylenes:



, (33)

where R′ = C_6H_5 and R = CH_3 or C_6H_5.

The conversion of disubstituted 7-silanorbornadiene, which yields $\ddot{Si}(CH_3)_2$ at low temperatures, also merits attention[157]:



. (34)

This method combines the utilisation of mild process conditions with the formation of the least reactive side products.

Attempts have been made to use the adduct of 1,1,-dimethyl-2,5-diphenyl-1-silacyclopentadiene with tolane for the same purposes[157]. However, the adduct not only eliminates dimethylsilylene but also dissociates simultaneously.

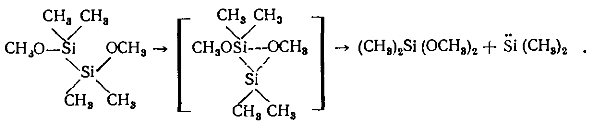
3. Thermal decomposition of polysilanes. The studies by Atwell and coworkers have shown that the most convenient and the most general source of organic silylenes is the thermolysis of alkoxymethylpolysilanes[2,158–162], for example:

$$(CH_3O)_6Si_2 \xrightarrow{175^\circ} (CH_3O)_4Si + \ddot{Si}(OCH_3)_2 \quad ; \tag{35}$$

$$CH_3(CH_3O)_2SiSi(OCH_3)_2CH_3 \xrightarrow{200^\circ} CH_3Si(OCH_3)_3 + \ddot{Si}(OCH_3)CH_3 \quad . \tag{36}$$

It was noted that, with increase of the number of alkoxy-groups, the thermolysis takes place at lower temperatures. These reactions can also be carried out in the gas phase. Following the development of this procedure, organic silylenes became readily available and have been the object of numerous interesting investigations.

The thermolysis of alkoxypolysilanes is a typical example of α-elimination:



. (37)

It has been reported that substituted disilanes $(CH_3)_3SiSi(CH_3)_2X$, where X = Cl, OC_6H_5, or C_6H_5, undergo similar reactions[163] and it is of interest that pentamethyldisilane is also apparently an effective donor of $\ddot{Si}(CH_3)_2$. Presumably, all the methyldisilanes $(CH_3)_{6-x}.Si_2H_x$, where $x = 1 - 6$, and naturally also the similar alkylpolysilanes undergo thermal decomposition into silylene and silane[76] by the intermolecular transfer of a hydrogen atom discussed above.

The pyrolysis of cyclic and linear polymers having the general formula $[Si(CH_3)_2]_n$, where $n > 3$, also leads to the formation of dimethylsilylene[153,164]. However, the yield of its adducts with various trapping agents is low (1–6%).[1,164]

2. OTHER ENERGY SOURCES IN THE SYNTHESES OF SILYLENES

A. The Silent Electric Discharge

The silent electric discharge in the vapours of silane and some of its derivatives has been found[165–173] to result in the formation of silylenes, the mechanism of which is believed to be described by equations similar to those discussed above:

$$SiX_4 \rightarrow \ddot{Si}X_2 + X_2 \quad , \tag{14}$$

where X = Cl,[167–169] F,[170,171] or H[165,166,172] and

$$CH_3SiH_3^{173} \rightarrow CH_3\ddot{Si}H + H_2 \quad ; \tag{11}$$

$$\rightarrow \ddot{Si}H_2 + CH_4 \quad . \tag{12}$$

At the same time decomposition under the influence of the electric discharge is a more complex process than pyrolysis, since it is accompanied by the formation of various charged and neutral species.

This method has not assumed preparative importance and it has been used for spectroscopic studies only.

B. Photolysis

The photochemical method for the generation of silylenes has developed considerably in recent years. The search for convenient sources of silylenes for both spectroscopic investigations and for preparative purposes has continued. Among the compounds investigated, various silanes, whose Si–H bonds are readily photodissociated, have found extensive applications. Flash photolysis of halogenosilanes has proved a very promising procedure for recording highly resolved absorption spectra of halogenosilylenes Their formation is evidently due to the following reaction:

$$H_3SiX \xrightarrow{h\nu} H\ddot{Si}X + H_2 \tag{38}$$

where X = Cl, Br,[174] or I.[175]

$\ddot{Si}H_2$, obtained in the photochemical decomposition of silane, has been identified similarly[176–178]. The vacuum ultraviolet photolysis[178] of silanes leads to the formation of silyl radicals and silicon atoms in addition to silylene.

The mercury-sensitised photochemical decomposition of silane evidently involves initial processes in which silyl radicals and silicon atoms are formed together with silylene via the reaction[179–182]:

$$Hg(^3P_1) + SiH_4 \rightarrow \ddot{S}iH_2 + 2H + Hg(^1S_0) \quad . \qquad (39)$$

However, it is interesting to note that all the methylsilanes are capable of decomposing under these conditions via a radical pathway involving the dissociation of a single Si–H bond[181,182], while silyl radicals disproportionate with formation of silylenes only to a slight extent.

The photolysis of alkylsilanes under the influence of vacuum ultraviolet proceeds via the molecular elimination mechanism and thus constitutes a convenient source of silylenes, which are generated via reactions analogous to reactions (11) and (12):[183–185]

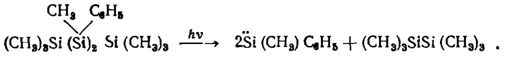
$$CH_3SiH_3 \xrightarrow{1470 Å} \begin{cases} \rightarrow CH_3\ddot{S}iH + H_2 \ ; \\ \rightarrow H_2\ddot{S}i + CH_4 \ . \end{cases}$$

The photochemical decomposition of dimethyl- and trimethyl-silanes proceeds similarly, although less efficiently[186].

A satisfactory method for the synthesis of dichloro-[187] and difluoro-silylenes[188] to be used in spectroscopic studies is the vacuum ultraviolet photolysis of dichloro- and difluoro-silanes. It is suggested that the $\ddot{S}iF_2$ obtained by this procedure is purer than the product synthesised by Timms' method[145].

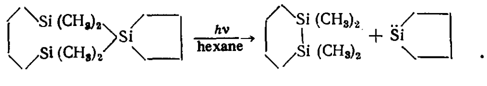
The photochemical method can be used to synthesise silylenes with organic substituents. Interesting possibilities in the synthesis of such silylenes arise on photolysis of substituted cyclic[189–191] or linear[191–195] polysilanes, for example:

$$[(CH_3)_2Si]_6 \xrightarrow{h\nu} \ddot{S}i(CH_3)_2 + [(CH_3)_2Si]_5 \ ; \qquad (40)$$



$$(CH_3)_3Si\underset{}{\overset{CH_3\ C_6H_5}{(Si)_2}}Si(CH_3)_3 \xrightarrow{h\nu} 2\ddot{S}i(CH_3)C_6H_5 + (CH_3)_3SiSi(CH_3)_3 \ . \qquad (41)$$

A very promising method for the preparation of silylenes with various substituents involves modification of the substituent at the central silicon atom in 1,2,3-trisilacycloheptane[195], which makes it possible to obtain new, unusual silylenes, for example a cyclic silylene from spirotrisilane:



(42)

C. Nuclear Reactions

Together with the methods indicated above, the recently developed method for the synthesis of silylenes with the radioactive ^{31}Si isotope has assumed considerable importance. The ^{31}Si atoms ($\tau_{1/2} = 2.62$ h) generated by the nuclear reaction $^{31}P(n, p)^{31}Si$ (on bombarding a phosphorus compound with fast neutrons) acquire energies corresponding to their chemical reactions as neutral species and their interaction with phosphine[196–202] or silane[196–198,200] apparently result in the formation of silylenes:

$$^{31}\cdot\dot{\underset{\cdot}{S}}i\cdot \xrightarrow{PH_3} {}^{31}\ddot{S}iH_2 \ , \qquad (43)$$

$$^{31}\cdot\dot{\underset{\cdot}{S}}i\cdot \xrightarrow{SiH_4} H^{31}\ddot{S}iSiH_3 \ . \qquad (44)$$

^{31}Si atoms can interact similarly with phosphorus trifluoride, forming difluorosilylene[203]:

$$^{31}\cdot\dot{\underset{\cdot}{S}}i\cdot + PF_3 \rightarrow {}^{31}\ddot{S}iF_2 \quad . \qquad (45)$$

Quite recently this method made it possible to show that $^{31}\ddot{S}iH_2$ exists in the triplet state to the extent of 80%.[199,202]

III. CHEMICAL PROPERTIES OF SILYLENES

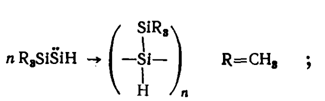
Before discussing the chemical properties of silylenes, the large number of experimental data concerning their physical properties should be noted. Investigators in this field have devoted most attention in the last five years to the examination of the molecular parameters of the species, the knowledge of which is necessary for the prediction of their chemical properties. The results of such studies have been reflected in recently published reviews[14,204] and papers[205–208].

We shall examine the chemistry of silylenes in accordance with their three characteristic intermolecular reactions—polymerisation, insertion in single bonds, and addition to multiple bonds. One should note immediately that, since data for the mechanism of the insertion of silylenes into single bonds are lacking, inferences about the nature of the insertion reaction are drawn mainly on the basis of the structure of the final products and are therefore frequently arbitrary.

The intermolecular reactions of the majority of silylenes can occur at elevated temperatures (in both gas and liquid phases) and at low temperatures on cocondensation with trapping agents. The majority of the reactions of difluorosilylene have little in common with those of other silylenes. The higher stability of $\ddot{S}iF_2$ in the gas phase compared with other silylenes[145,146,209–211] made it a convenient object of study. It is known, that with rare exceptions[140,144,209], difluorosilylene is inert in the gas phase[4,146,209]. Because of this and because its chemistry has been frequently discussed[4,6,8,9,212], less attention is devoted to it in the present review.

1. POLYMERISATION

In the absence of active trapping agents, silylenes are polymerised with formation of polysilanes:



$$nR_3Si\ddot{S}iH \rightarrow \left(\begin{array}{c} SiR_3 \\ | \\ -Si- \\ | \\ H \end{array}\right)_n \qquad R{=}CH_3 \quad ; \qquad (46)$$

$$n\ddot{S}iX_2 \rightarrow (SiX_2)_n \quad . \qquad (47)$$

This property is characteristic of any silylene, i.e. when X = Cl,[22,44,83,139,141,142,149,167] Br,[83,135,137,149] H,[79,93,95,166] I,[27,81,82,138,149,213] CH_3,[150,154,155,162,164,190] etc.

Difluorosilylene does not form polymers in the gas phase. Its reactivity increases greatly on cocondensation with other reagents at the temperature of liquid nitrogen (−196°C).[4,146,209,212,214–221] This unusual effect may be due to the stepwise polymerisation of difluorosilylene. $\ddot{S}iX_2$ polymerises in the condensed phase with formation of biradicals of the type $\ddot{S}iF_2–(SiF_2)_n–\ddot{S}iF_2$ (where $n = 0, 1, 2, ...$) and these are in fact the reactive species[4,146,222–230]. Experiments in an argon matrix showed that polymerisation begins at approximately 35 K.[146,224]

Silicon monoxide, a very reactive silylene, polymerises rapidly even at 30 K,[130,233] forming dimers and oligomers with a bridging oxygen atom[9,130]. Owing to the causes indicated above and in contrast to other silylenes, the reactions of $\ddot{Si}F_2$ and $\ddot{Si}O$ with acceptors are investigated exclusively by the cocondensation method.

2. REACTIONS INVOLVING INSERTIONS IN SINGLE BONDS

Until recently, the ability of silylenes to form products of insertion in Si–H, E–X (E = Si, P, B, or C and X = halogen), Si–O, and Si–N bonds only were believed to be reliably established[2,76,229]. The research on insertion reactions has recently developed on a large scale, which has tended to extend current ideas about the synthetic possibilities of silylenes. Together with a description of the familiar general reactions of silylenes, we have therefore devoted much attention in the present section to new data on their properties.

The Insertion of Silylenes in Si–X Bonds (X = Halogen or OCH_3)

The formation of perhalogenopolysilanes as products of the thermal interaction of tetrahalogenosilanes with silicon [reaction (1)] involving the formation of dihalogenosilylenes which is evidently followed by their insertion in the Si–X (X = halogen) bond, has been known for a long time:

$$(n-1)\ddot{Si}X_2 + SiX_4 \rightarrow Si_nX_{2n+2} \quad . \tag{48}$$

These reactions occur in gas[25,35,44] and liquid[5,6] phases and have been thoroughly investigated; a number of perhalogenopolysilanes with n = 2–6 for X = Cl [136,139] and n = 2–5 for X = Br [136] have been obtained on their basis. The reactions of organosilylenes with alkoxypolysilanes have also been thoroughly investigated[2,158,160]. The formation of products of the $CH_3O[Si(CH_3)_2]_nOCH_3$ series in the thermolysis of *sym*-dimethoxytetramethyldisilane can be accounted for by the insertion of dimethylsilylene in the Si–O bond and not the Si–Si bond[3,161,162]. The dimethylsilylene obtained by photolysis is likewise not inserted in the Si–Si bond of 1,2-diethyltetramethyldisilane[193].

Although the possibility of the insertion of $\ddot{Si}H_2$ in the Si–Si bond has been postulated in certain recently published studies[95,100,198], nevertheless convincing confirmation of such behaviour has not been obtained for other silylenes. It is interesting that the insertion of organic silylenes (obtained by the thermolysis of alkoxypolysilanes) in the Si–O bond of an alkoxymonosilane does not compete with the analogous insertion into an alkoxypolysilane[161]. However, the absence of alkoxypolysilanes, the reaction of photolytically generated $\ddot{Si}(CH_3)_2$ with dimethyldimethoxysilane[190] proceeds with formation (in a high yield) of products resulting from insertion in the Si–O bond:

$$\ddot{Si}(CH_3)_2 + (CH_3O)_2Si(CH_3)_2 \rightarrow CH_3O\,[Si(CH_3)_2]_nOCH_3 \; ; \quad n = 2.3 \quad . \tag{49}$$

Insertion in the Si–O bond has also been postulated in the cocondensation of difluorosilylene with trimethylmethoxysilane, but the initial reaction product $(CH_3)_3.SiSiF_2OCH_3$ was not isolated, apparently owing to its further transformations[228].

Thus, although insertion in the Si–X bond (X = halogen or O) is a fairly general reaction for all silylenes, usually accompanying their formation, its further investigation is required in order to explain the different reactivities of such bonds.

Insertion in E–X Bonds (E = B, P, or C and X = F or Cl)

One of the first reactions of silylenes investigated, the interaction of SiF_2 with boron trifluoride[209,222,224,231], belongs to this type. It was established that the reaction does not occur in the gas phase, while in the condensed phase (with consecutive condensation initially of boron trifluoride and then of difluorosilylene) a number of compounds $SiF_3(SiF_2)_nBF_2$ (n = 1–4) are formed with an overall yield of 10–20%. The simplest member with n = 1 was not detected for a long time among the perfluoroborosilanes formed. Difluoro(trifluorosilyl)borane was isolated quite recently with simultaneous condensation of the reactants[232]:

$$\ddot{Si}F_2 + BF_3 \xrightarrow{\text{cocondensation}} SiF_3BF_2 \tag{50}$$

the yield being higher when $\ddot{Si}F_2$ is obtained by passing SiF_4 over silicon carbide at 1850°C. It is suggested that short-lived species (possibly an excited form of $\ddot{Si}F_2$) are formed together with the long-lived $\ddot{Si}F_2$ species.

The interaction of $\ddot{Si}Cl_2$, obtained by the reaction of silicon and silicon tetrachloride [reaction (28)], with E–Cl bonds (E = B, P, or C) [141,142] has been suggested as a general method for the synthesis of compounds with an E–SiCl linkage[234–236], for example:

$$\ddot{Si}Cl_2 + BCl_3 \xrightarrow{\text{cocondensation}} Cl_3SiBCl_2 \quad . \tag{51}$$

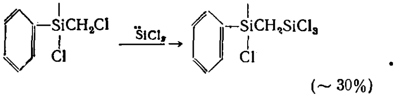
In all the experiments of this kind, the yield has been fairly low (approximately 10%). The analogous interaction of $\ddot{Si}Br_2$ with BF_3 is complicated by the exchange of halogens[2].

The gas-phase reactions of dichlorosilylene with the C–Cl bond of organic halides are of considerable preparative interest:

$$\ddot{Si}Cl_2 + CH_3Cl \rightarrow CH_3SiCl_3^{85,92} \quad ; \tag{52}$$

$$ArCH_2Cl \xrightarrow{\ddot{Si}Cl_2} ArCH_2SiCl_3^{68,92} \; (30\text{—}35\%) \quad , \tag{53}$$

Ar = phenyl or naphthyl



(54)

(~ 30%)

At first sight the interaction of $\ddot{Si}F_2$ with trifluoroiodomethane[237–239] also leads to the product resulting from insertion in the C–F bond (the main product is the compound with n = 1):

$$CF_3I + \ddot{Si}F_2 \xrightarrow{\text{cocondensation}} CF_3(SiF_2)_nI \quad . \tag{55}$$

However the additional formation of further two types of compounds suggests a more complex mechanism with formation in the first stage of the radical $\dot{Si}F_2I$ and its subsequent reactions.

The results of a study of the reaction of silicon monoxide with 1-bromo- or 1-chloro-butane and bromo- or chlorobenzene suggested that the main reaction involves insertion in the C–halogen bond[9]:

$$C_4H_9Cl \xrightarrow{\ddot{Si}O} C_4H_9(SiO)_6Cl \quad . \tag{56}$$

However, the product of the reaction of monomeric silicon monoxide was not detected. The possibility of the occurrence of the above reaction for difluorosilylene may be demonstrated by the interaction with fluoro-derivatives of benzene[216] and alkenes[217,218]:

$$\ddot{Si}F_2 + C_6F_6 \xrightarrow{\text{cocondensation}} C_6F_5SiF_3 + C_6F_4(SiF_3)_2, \tag{57}$$

$$\ddot{Si}F_2 + n\text{-}C_6H_4F_2 \xrightarrow{\text{cocondensation}} n\text{-}FC_6H_4SiF_3 \tag{58}$$

$$\ddot{S}iF_2 + H_2C{=}CF(CH_3) \xrightarrow{\text{cocondensation}} H_2C{=}C(CH_3)SiF_3 + H_2C{=}C(CH_3)Si_2F_5 \quad . \tag{59}$$

It is suggested that the attacking species is monomeric difluorosilylene. Thus, when the compounds contain the C–F bond, the latter is evidently attacked more readily than the C=C bond by monomeric $\ddot{S}iF_2$ with formation of the SiF_3 group.

Insertion in Halogen, Hydrogen Chloride, and Hydrogen Molecules

Silylenes are easily inserted in halogen–halogen bonds[76]:

$$\ddot{S}iCl_2 + X_2 \xrightarrow{\Delta} X_2SiCl_2, \tag{60}$$

where X = I, Br,[35] or Cl.[24];

$$\ddot{S}iF_2 + X_2 \xrightarrow{\Delta} F_2SiX_2 \text{ (yield up to 70\%)}, \tag{61}$$

where X = Br, Cl,[144] or I.[144,240] It must be emphasised that the reaction with halogens [reaction (61)] is so far the only example of a gas-phase reaction of difluorosilylene, which is apparently involved in the monomeric form.

Insertion in the H–Cl bond was postulated as early as 1953 [44] and was subsequently confirmed[34,46]:

$$\ddot{S}iCl_2 + HCl \rightarrow HSiCl_3 \quad . \tag{62}$$

The reaction of photolytically generated dimethylsilylene is typical[191]:

$$\ddot{S}i(Me_2) + HCl \xrightarrow{h\nu} (CH_3)_2SiHCl \text{ (yield 72\%).} \quad . \tag{63}$$

The intermediate $\ddot{S}iCl_2$ may be inserted in the H–H bond[44]:

$$\ddot{S}iCl_2 + H_2 \xrightarrow{\Delta} H_2SiCl_2 \quad . \tag{64}$$

Insertion in E–H Bonds (E = Si, Ge, O, N, or S)

The insertion of silylenes in the Si–H bond, first observed by Skell and Goldstein[150,151],

$$\underset{}{\ddot{S}i(CH_3)_2 + (CH_3)_3SiH \xrightarrow{260^\circ} \underset{(\sim 30\%)}{(CH_3)_3SiSi(CH_3)_2H}} \quad , \tag{65}$$

has been widely used both to demonstrate the intermediate formation of various silylenes and to obtain new compounds with the Si–Si bond[8,75,79,94–100,241], for example:

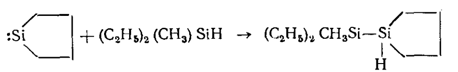
$$CH_3\ddot{S}iH + CH_3SiH_3 \xrightarrow{\Delta} CH_3SiH_2SiH_2CH_3 \quad ; \tag{66}$$

$$\ddot{S}iH_2 + Si_3H_8 \xrightarrow{\Delta} \text{n- and iso-}Si_4H_{10}; \tag{67}$$

$$H\ddot{S}iSiH_3 + Si_3H_8 \xrightarrow{\Delta} \text{n- and iso-}Si_5H_{12}. \tag{68}$$

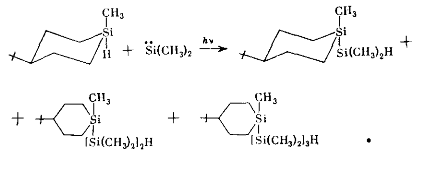
Organic silylenes obtained photochemically are also readily inserted in the Si–H bond[183–186,189,190,192–194]:

$$\ddot{S}i(CH_3)_2 + (C_2H_5)_2(CH_3)SiH \rightarrow (C_2H_5)_2CH_3Si{-}Si(CH_3)_2H \quad ; \tag{69}$$



. (70)

It has been shown by NMR [242] that the insertion of dimethylsilylene in the Si–H bond of *cis*- or *trans*-4-t-butyl-1-methyl-1-silacyclohexane proceeds *cis*-stereospecifically, as for dichlorocarbene[243]:



(71)

The observed conservation of configuration in the insertion reaction (71) is undoubtedly associated with a three-centre mechanism involving direct electrophilic attack by dimethylsilylene on the Si–H bond.

The silicon atoms obtained by thermal evaporation [see reaction (26)] are inserted in the Si–H bond with formation of silylenes[102,104–106]:

$$\cdot\dot{\underset{\cdot}{S}}i\cdot + \cdot R_3SiH \rightarrow R_3Si{-}\ddot{S}iH \quad , \tag{72}$$

which involves a further insertion in its turn:

$$R_3Si{-}\ddot{S}iH + R_3SiH \rightarrow R_3SiSiH_2SiR_3 \quad . \tag{73}$$

Similarly ^{31}Si Atoms [see reaction (43)] form silylenes which are subsequently involved in a secondary process with formation of radioactive disilane[196,197] and trisilane[198]:

$${}^{31}\ddot{S}iH_2 + SiH_4 \rightarrow H_3{}^{31}Si{-}SiH_3 \quad ; \tag{74}$$

$${}^{31}\ddot{S}iH_2 + H_3SiSiH_3 \rightarrow H_3{}^{31}SiSiH_2SiH_3 \quad . \tag{75}$$

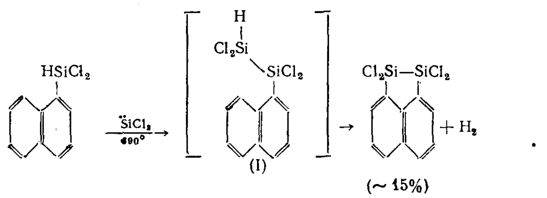
The ratio of trisilane and disilane occurring in this process enabled the authors to postulate the competing insertion of silylene in the Si–Si bond[198]. A similar hypothesis has been put forward also in studies of the pyrolysis of disilane[25] and trisilane[100]. The available data concerning the different bond strengths in disilane and silane[244] suggest the need for further research in order to account for the observation.

The reactions involving the insertion of silylene $\ddot{S}iH_2$ in the Si–H bond have been most fully investigated. Thus experiments on the joint pyrolysis of disilane and all methylsilanes have shown that $\ddot{S}iH_2$ is undoubtedly inserted exclusively in the Si–H bond of the reactant[95]. Measurements of the relative rates of insertion of $\ddot{S}iH_2$ in the E–H bonds (E = Si, Ge, or P) at 350°C have shown that the reactivity per E–H bond decreases in the following sequence[100]:

$$(CH_3)_3SiH > Si_2H_6 > (CH_3)_2SiH_2 > CH_3SiH_3 > SiH_4 > CH_3GeH_3 \quad .$$

The differences between the rates of insertion can be explained from the standpoint of the hydride nature of the E–H bond (i.e. they are correlated with the negative charge on the attacking hydrogen atom). This is particularly evident in the reaction with methylphosphine, where the hydrogen atom has a positive charge and the insertion of silylene is not observed[100,241].

The formation of a heterocyclic compound with an Si–Si bond, namely 1,1,2,2-tetrachloro-1,2-disila-acenaphthene, by the pyrolysis of trichlorosilane or hexachlorodisilane with dichloro-α-naphthylsilane, probably proceeds via a mechanism involving intramolecular dehydrocyclisation of compound (I)—the primary product of the insertion of dichlorosilylene in the Si–H bond[63]:



. (76)

The interaction of difluorosilylene with germane led to the formation of products of the type $GeH_3(SiF_2)_nH$, where $n = 1$–3.[215] The main product with $n = 1$ may be regarded as the product of the insertion of monomeric $\ddot{S}iF_2$ in the Ge–H bond:

$$\ddot{S}iF_2 + GeH_4 \xrightarrow{\text{cocondensation}} GeH_3SiF_2H \quad . \tag{77}$$

At the same time, it was suggested that germane attacks the silylene chains in $\dot{\mathrm{Si}}F_2(SiF_2)_nSiF_2$, abstracting fragments containing 1, 2, and 3 silicon atoms.

The reactions of silylenes with E–H bonds, where E = O, N, or S, have been less thoroughly investigated. Several investigations have dealt with the interaction of silylenes with alcohols[9,161,245] and water[9].

$$\ddot{\mathrm{Si}}(OCH_3)_2 + CH_3OH \xrightarrow{\Delta} HSi(OCH_3)_3 \;; \qquad (78)$$

$$4\ddot{\mathrm{Si}}O + C_2H_5OH \xrightarrow{\text{cocondensation}} (C_2H_5O)H(SiO)_4 \;. \qquad (79)$$

The reaction of difluorosilylene with methanol proceeds in a much more complex manner[245]. It is suggested that it involves monomeric $\ddot{\mathrm{Si}}F_2$, which is inserted in the O–H bond, but the product formed reacts further with the excess of alcohol, forming difluorodimethoxysilane. The most likely pathway of the reaction with water appears to be insertion of monomeric $\ddot{\mathrm{Si}}F_2$ with subsequent condensation of the product:

$$\ddot{\mathrm{Si}}F_2 + H_2O \xrightarrow{\text{cocondensation}} HF_2SiOH \;; \qquad (80)$$

$$2HF_2SiOH \rightarrow HF_2SiOSiF_2H + H_2O \;. \qquad (81)$$

As in the reaction of $\ddot{\mathrm{Si}}F_2$ with oxygen[4,222,246], polymeric oxides are not formed in this case and the biradicals are not therefore involved in the reaction mechanism.

The interaction of silicon monoxide with ammonia[9] led to the formation of a new compound having the approximate composition $NH_3(SiO)_4$.

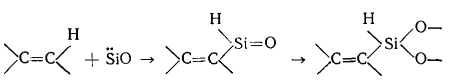
The insertion of $\ddot{\mathrm{Si}}F_2$ in the S–H bond of hydrogen sulphide was reported earlier[2]:

$$\ddot{\mathrm{Si}}F_2 + H_2S \xrightarrow{\text{cocondensation}} HF_2SiSH \;. \qquad (82)$$

Later detailed studies[219,238] showed that the process does not proceed in a single stage and evidence concerning the validity of the exclusion of the dimerisation stage was not obtained.

New Silylene Insertion Reactions

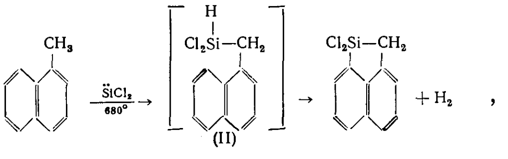
The results of studies demonstrating the ability of dichlorosilylene[68,90,92,247–249] and silicon monoxide[9,130] to interact with a wide variety of carbon–hydrogen bonds are perhaps the most interesting. It should be noted that these processes, which are the most characteristic reactions of carbenes, were completely unknown for silylenes until recently. Alkanes, anthracene, and benzene have been used in the reactions with silicon monoxide. The structure of the compounds obtained corresponds in all cases to the products resulting from insertion in the C–H bond. Furthermore, it was found that, apart from adding to multiple bonds, silicon monoxide is also "inserted" in the C–H bonds of alkenes and alkynes:



(83)

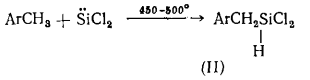
The products contain 2–3 moles of silicon monoxide per mole of alkene. Thus polymerisation evidently competes with the reaction involving the alkene, as in other cases.

The study of the gas-phase reaction of dichlorosilylene with C–H bonds[68,90,92] elucidated several important factors. After the first investigations indicating the ability of $\ddot{\mathrm{Si}}Cl_2$ to form products resulting from insertion in the C_{alk}–H bond of α-methylnaphthalene[65],



(84)

it was found that this reaction is common to all methylsubstituted aromatic hydrocarbons and heterocycles[91,92,247–249]

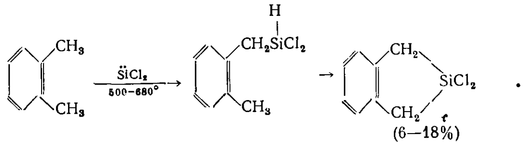


$$ArCH_3 + \ddot{\mathrm{Si}}Cl_2 \xrightarrow{450-500^\circ} \underset{(II)}{ArCH_2SiCl_2H} \;, \qquad (85)$$

where Ar = phenyl, *o*- and *p*-tolyl, *p*-biphenylyl, α- and β-naphthyl, 2- and 3-thienyl, etc.

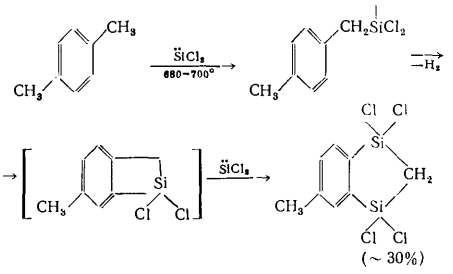
The absence of primary $\ddot{\mathrm{Si}}Cl_2$ insertion products [compounds of type (II)] in the experiments carried out at 680°C and the low yield under the conditions of reaction (85) are due to the increased tendency of these compounds to undergo radical reactions[92].

In the presence of the given substituent in the *ortho*-positions of the initial compounds, the interaction of dichlorosilylene with the C–H bond may be accompanied by subsequent intramolecular cyclisation[91,92]:



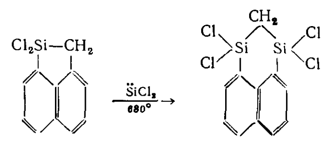
(86)

Another feature of dichlorosilylene observed in these reactions, which is of great preparative importance, is its ability to be "inserted" in the C_{ar}–C_{alk} bond of strained rings[90,92], i.e. the reaction on which the synthesis of heterocyclic compounds with two silylene groups is based[248,249]:



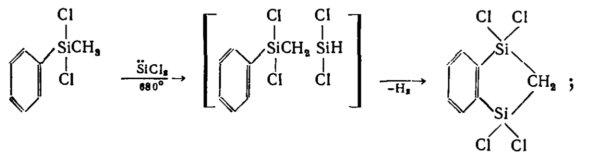
(87)

The available literature data concerning the unusual strength of the Si–C bond in pyrolytic syntheses serves as a basis for this mechanism[250]. Furthermore, pyrolysis of the primary insertion products [of the type of compound (II)] in the presence of a dichlorosilylene donor leads to the same heterocycles[92]. It is noteworthy that a reaction of this type, expansion of a five-membered ring to a six-membered ring as a result of the formal insertion of $\ddot{\mathrm{Si}}Cl_2$ in the C_{ar}–C_{alk} bond, has been observed also in another instance[68,92]:

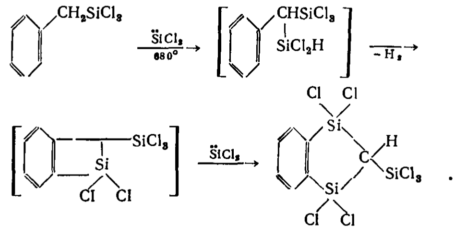


(88)

Studies on the interactions of dichlorosilylenes with other C–H bonds are only just beginning. In particular, the ability of $\ddot{\mathrm{Si}}Cl_2$ to be "inserted" in the C–H bond involving the α-carbon atom attached to the silicon atom has been confirmed by the formation of the corresponding heterocycle as a result of gas-phase reactions[92,249]:

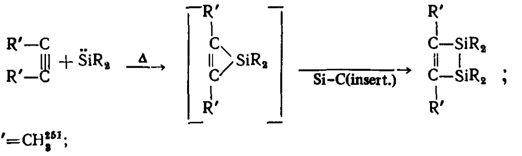


(89)



(90)

Among the latest communications, those presenting data suggesting the insertion of dimethylsilylene[251] and dichlorosilylene[92] in the Si–C bond of a silicon-containing heterocycle are of greatest interest. This hypothesis was put forward on the basis of a study of the products of the reactions of silylenes with substituted acetylenes. One of the possible mechanisms of the formation of the observed four-membered heterocycle with an Si–Si bond, put forward by analogy with dichlorocarbene[252,253], is the insertion of $\ddot{\mathrm{Si}}(\mathrm{CH_3})_2$ and $\ddot{\mathrm{Si}}\mathrm{Cl_2}$ in the Si–C bond of silacyclopropene formed as an intermediate in the first stage of the reaction (see below):



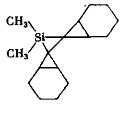
(91)

(a) $R=R'=CH_3$[251];
(b) $R=Cl$, $R'=C_6H_5$[92] .

Summarising the foregoing findings, one may conclude that the insertion reactions investigated are at present at the stage of rapid development. In this sense, the gas-phase method must be regarded as one of the most promising procedures, the wide-scale employment of which will lead to the discovery of hitherto unknown properties of silylenes.

3. THE ADDITION OF SILYLENES TO MULTIPLE BONDS

The interaction with unsaturated compounds is one of the most characteristic reactions of silylenes. Unsaturated compounds are of particular interest as trapping agents for silylenes, since they make it possible to approach the synthesis of hitherto unknown silacyclopropanes and silacyclopropenes. All the attempts to isolate three-membered heterocycles with a silicon atom in the ring, which are evidently extremely labile, have been unsuccessful[154,164,254]. Such cyclic systems can probably be stabilised by increasing the degree of substitution at the ring carbon atoms. This is confirmed satisfactorily by the synthesis of the first relatively stable silacyclopropanes by the organometallic method[255], for example:



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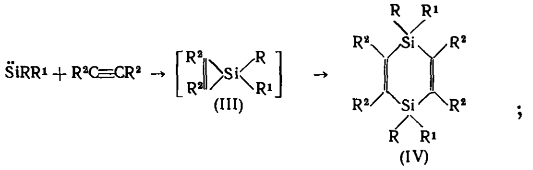
Interaction with Alkynes

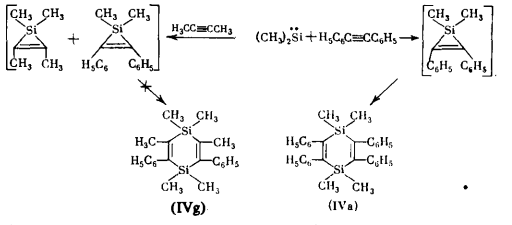
Among the large number of unsaturated "trapping agents" for silylenes which have been investigated, alkynes are the most effective. The formation of silacyclopropene in the reaction of dimethylsilylene with diphenylacetylene was reported in 1961.[152,153] Subsequent studies on this reaction[256–260] showed that the product has a dimeric structure and is tetraphenyldisilacyclohexa-2,5-diene (IVa). Since then research on the reactions of a wide variety of silylenes with alkynes has developed on a wide scale and the reaction is now used to obtain chemical proof of the formation of silylenes:



(92)

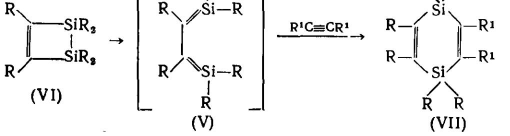
(a) $R=R^1=CH_3$, $R^2=C_6H_5$[1,152,153,155,158–160];
(b) $R=CH_3$, $R^1=OCH_3$, $R^2=C_6H_5$[160,261];
(c) $R=CH_3$, $R^1=OCH_3$, $R^2=CH_3$[2,261];
(d) $R=CH_3$, $R^1=OCH_3$, $R^2=H$[2,261,262] ;
(e) $R=R^1=Cl$, $R^2=H$[89–92,263,288] ;
(f) $R=R^1=Cl$, $R^2=C_6H_5$[89–92,263,288] .

The mechanism of this reaction is still obscure. Existing views can be summarised as follows. The majority of investigators believe that the primary step is the addition of silylene to the triple bond of the alkyne with formation of compound (III), but its subsequent fate is represented in different ways. The studies by Atwell and Weyenberg[159] of the reaction of dimethylsilylene with a mixture of diphenylacetylene and but-2-yne, which did not yield 3,5-diphenyldisilacyclohexadiene (IVg), made it possible to exclude from further consideration the previously proposed mechanism involving the π-dimerisation of compound (III). We examined the possibility of the mechanism involving a kind of dimerisation of silacyclopropene (III) with dissociation of the Si–C bond:



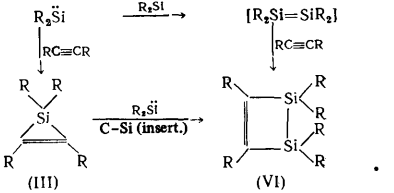
(93)

A mechanism for the formation of disilacyclohexadienes, including compound (VII), via the Diels-Alder addition of acetylene to 1,4-disilabuta-1,3-diene (V) has been proposed recently[264]:

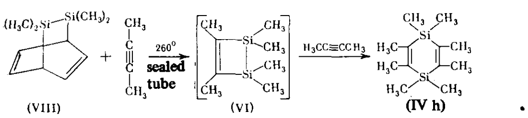


(94)

It is suggested that the diene (V) is formed from 1,2-disilacyclobutene (VI) and the authors believe that in the case where $R \neq R^1$ this explains the absence of the isomer (IVg) in the experiment with mixed actylenes. Compound (VI) can be formed in several ways: (1) by the insertion of silylene, discussed above, in the Si–C bond of the intermediate silacyclopropene; (2) by the dimerisation of silylene accompanied by the addition of the resulting disilylene to acetylene:

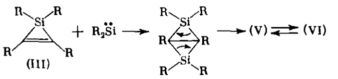

(95)

The latter mechanism is supported by the formation of disilacyclohexadiene (IVh) in 20% yield in the reaction between the donor $[(CH_3)_2Si{=}Si(CH_3)_2]$ [265] (VIII) and but-2-yne:

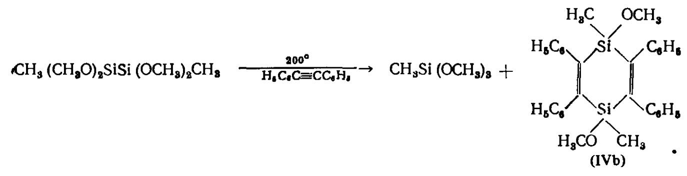

(96)

If, however, the reaction of compound (VIII) with but-2-yne in the gas phase does not lead to the formation of disilyacyclohexadiene (IVh), which may indicate different contributions of this mechanism to the reaction of silylenes with alkynes depending on its conditions. At any rate, the thermolysis of compound (VI) in the presence of but-2-yne (sealed tube, 225°C, 18 h) does indeed lead to compound (IVh) in 31% yield.

Finally Barton and Kilgour[264] also believe that the addition of silylene to the double bond of silacyclopropene with subsequent thermal rearrangement of the molecule to compound (V) is likely:


(97)

Among the studies of the above reaction, one must distinguish those which have led to the formation of disilacyclohexadienes with functional groups at the silicon atom[89–92,160,261–263]. The first example is the synthesis of the tetraphenyl-substituted 1,4-dimethoxy-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (IVb) in 50% yield[160,261]:


(98)

However, the corresponding tetramethoxy-derivatives could not be obtained by a similar procedure from diphenylacetylene and hexamethoxydisilane[159,160].

The most promising procedure involves carrying out the above reactions in the gas phase[89–92,261–263]. The yield of methoxymethyldisilacyclohexadiene (IVd) under the conditions of reaction (92) at 400°C was 60%.[261–262] The use of hexachlorodisilane and octachlorotrisilane in the reaction with alkynes (at 500–550°C) made it possible to obtain tetrachlorodisilacyclohexadiene (IVe) in yields up to 30% and its tetraphenyl derivative (IVf) in a yield of approximately 10%, which is of preparative interest for the synthesis of the previously inaccessible tetrafunctional derivatives of disilacyclohexa-2,5-diene. The stability of all the heterocycles (IV) synthesised on heating to the melting point is noteworthy. Furthermore, tetrachlorodisilacyclohexadiene (IVe) undergoes various reactions characteristic of the Si–Cl bond: methylation, and substitution of chlorine atoms by hydrogen and fluorine atoms with retention of the cyclic skeleton of the molecule. Timms' data[5] concerning the instability above 0°C of tetrachlorodisilacyclohexadiene, which he obtained by the reaction of dichlorosilylene with acetylene by the cocondensation method, must therefore be regarded as unreliable.

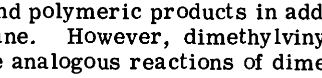
A low yield of tetrachlorotetraphenyldisilacyclohexadiene (IVf) may be associated with the insertion of $\ddot{Si}Cl_2$ in the Si–C bond of the intermediate diphenylsilacyclopropene (III) (see subsection 2 of Section III). It is interesting to note that, in the analogous reactions of acetylene and its derivatives with difluorosilylene, the formation of silacyclopropene derivatives has not been observed and the reactive species with respect to alkynes are the diradicals $\cdot(SiF_2)_2^{\cdot}$.[266–272]

A study of the interaction of silicon monoxide with alkynes[9] demonstrated the competition between two reactions: addition to the triple bond and insertion of $\ddot{Si}O$ in the C–H bond. The approximate composition of the solid product formed by the reaction with acetylene is $C_2H_2(SiO)_3$. The reaction with diphenylacetylene evidently results in the formation of the expected compounds $C_{14}H_{10}(SiO)_2$ having the disilacyclohexadiene structure.

Interaction with Alkenes

Various mixtures of products formed in the interaction of silylenes with ethylene in the gas or condensed phases have been reported in a number of studies[2,154,164,254]. The addition of dimethylsilylene to ethylene accompanied by the formation of dimethylvinylsilane has been achieved in the gas phase[254].

The addition of silylene (${}^{31}\ddot{Si}H_2$), obtained by the reaction of ${}^{31}Si$ atoms with phosphine, to silylene has been described[197] (see subsection 2 of Section II):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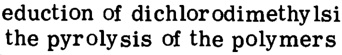
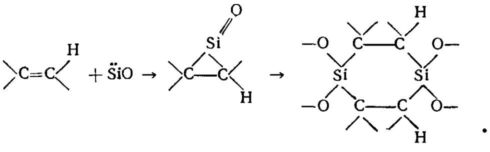
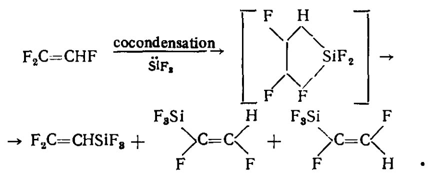

(100)

These results of the interaction of dimethylsilylene with ethylene in the liquid phase are interpreted in different ways. According to Atwell and Weyenberg[2], dimethylsilylene, obtained by the thermolysis of 7-silanorbornadiene [see reaction (33)], reacts with ethylene, forming cyclic and polymeric products in addition to dimethylvinylsilane. However, dimethylvinylsilane is not formed in the analogous reactions of dimethylsilylene formed by the reduction of dichlorodimethylsilane with lithium[154] or by the pyrolysis of the polymers $[Si(CH_3)_2]_n$ [164] see above). The possibility of error is associated with the low yield of volatile products in this reaction (overall yield less than 10%). The formation of cyclic products was postulated in the analogous experiments with silicon monoxide[9]:


(101)

In contrast to the reaction of difluorosilylene with ethylene, the cyclic products of which indicate the involvement of the polymeric species $\cdot(SiF_2)_n^{\cdot}$, the reactions with fluorinated derivatives of ethylene yield monosilanes[217,218], the formation of which is explained either by the insertion of $\ddot{S}iF_2$ in the C–F bond (see subsection 2 of Section III) or by the isomerisation of the intermediate silacyclopropane[4,218]:

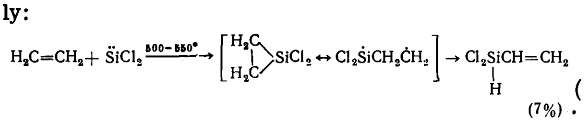


(102)

It has been reported recently[5,6] that the cocondensation of dichlorosilylene with propene (at –196°C) leads to the formation of the corresponding disilacyclohexane derivatives; the authors claim that, owing to the ease of insertion of $\ddot{S}iCl_2$ in the Si–Cl bond, it is difficult to avoid the formation of 1-trichlorosilyl-1,2-disilacyclohexane. However, attempts to demonstrate unambiguously the structure of the compounds obtained were not made.

In the light of these data, the results of studies on the gas-phase reactions of dichlorosilylene are of considerable interest. The joint pyrolysis of perchloropolysilanes and ethylene, which does not lead to the formation of cyclic compounds, is typical[92]. However, silicon-containing products are formed in an overall yield of approximately 70% in this case also.

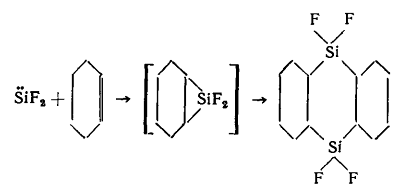
As in the instances described above, the mechanism involving the addition of dichlorosilylene to ethylene with formation of a labile adduct, the structural isomerism of which leads to dichlorovinylsilane, appears to be most likely:



(103)

The remaining organosilicon compounds [$Cl_3SiCH{=}CH_2$ (18%), $Cl_3SiC_2H_5$ (16%), $(H_2C{=}CH)Cl_2SiC_2H_5$ (20%), and $(C_2H_5)_2SiCl_2$ (10%)] are most probably the products of secondary reactions of the adduct of $\ddot{S}iCl_2$ and ethylene.

The addition of monomeric $\ddot{S}iF_2$ to cyclohexene[2] with subsequent dimerisation of silacyclopropane has been reported in a preliminary communication, but is not quoted in later reviews on the chemistry of difluorosilylene:



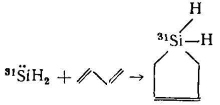
(104)

Reactions with Dienes and Polyenes

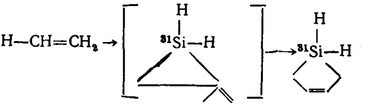
Conjugated dienes are the most reactive "trapping agents" for silylenes. Furthermore, the information in the review of Atwell and Weyenberg[2] about the addition of organic silylenes, generated by the thermolysis of alkoxydisilanes, to 2,3-dimethylbuta-1,3-diene can now be supplemented by the following new findings. These reactions proceed quite well also in the gas phase[161], where side reactions involving the dimerisation of the diene proceed to a negligible extent, and the yield of the main products is very high (approximately 60%).

It has been stated that monomeric $[^{31}Si]$ difluorosilylene, obtained by a nuclear reaction (see above), also reacts with butadiene to form 1,1-difluoro-1-$[^{31}Si]$silacyclopent-3-ene[203].

The first study on the addition of the silylene $^{31}\ddot{S}iH_2$ to buta-1,3-diene[199] showed that 80% of the silylene obtained by the nuclear reaction (43) is in the triplet state and 20% is in the singlet state[202]. The proposed mechanism for the formation of $[^{31}Si]$silacyclopent-3-ene presupposes the 1,4-addition of the triplet silylene and the 1,2-addition of the singlet silylene:

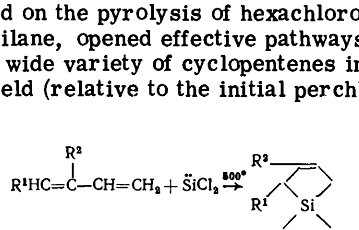


(105)



(106)

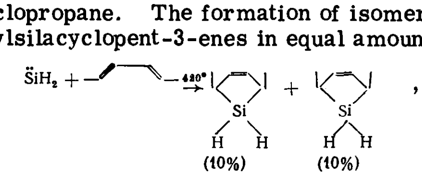
The syntheses of various mono- and bi-functional silacyclopentenes via intermediate silylenes such as $\ddot{S}i(CH_3)Cl$, $\ddot{S}i(CH_3)F$, and $\ddot{S}iCl_2$ have been described in the patent literature[274]. The method of synthesis of dichlorosilylene, based on the pyrolysis of hexachlorodisilane or octachlorotrisilane, opened effective pathways to the synthesis of a wide variety of cyclopentenes in almost quantitative yield (relative to the initial perchloropolysilane)[89-92,263]:



(107)

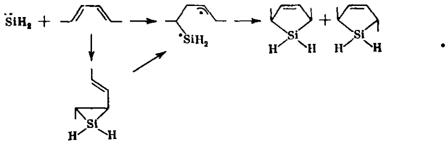
where R^1 = H or CH_3 and R^2 = H, CH_3, or Cl. It is noteworthy that the insertion of the dichlorosilylene in the C–Cl, C–H, and Si–Cl bond is observed in this case.

The silacyclopentenes obtained by reaction (107) are formally products of the 1,4-addition of dichlorosilylene, but one cannot rule out the possibility that dichlorosilylene initially attacks one of the double bonds of the diene with subsequent isomerisation of the intermediate vinylsilacyclopropane. The formation of isomeric 2,5-dimethylsilacyclopent-3-enes in equal amounts,



(108)

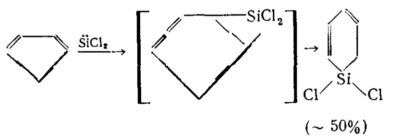
makes it possible to rule out the concerted 1,4-addition of silylene ($\ddot{S}iH_2$) to *trans*-2-*trans*-4-hexadiene[233], which should have led to the *cis*-product exclusively. This factor served as basis for the hypothesis of a biradical mechanism. The biradical can be obtained both as the primary adduct or as a result of the opening of the vinylsilacyclopropane ring[2,8]:



(109)

Reactions via the mechanism discussed above are evidently impossible for difluorosilylene[275] and silicon monoxide[9], the interaction of which with dienes in the condensed phase is accompanied by the formation of cyclic compounds containing Si_2F_4 and $(SiC)_2$ units. It is believed that the latter are the products of the 1,4-addition of dimeric biradicals.

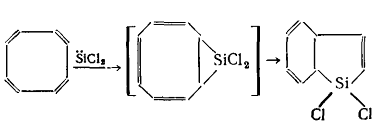
An interesting version of the reaction involves the addition of $\ddot{S}iCl_2$ to a cyclic diene (cyclopentadiene)[89-92,263]. This reaction probably proceeds via the addition of $\ddot{S}iCl_2$ to the double bond, the resulting intermediate adduct undergoing rearrangement in the next stage:



(110)

It is noteworthy that the synthesis of 1,1-dichloro-1-silacyclohexa-2,4-diene by other procedures is difficult, since these are mainly multistage syntheses with low yields producing an admixture of isomers which are difficult to separate[276].

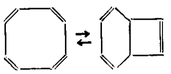
A non-conjugated cyclic polyene system such as cyclo-octatetraene is an interesting object of investigation[92]. The interaction of hexachlorodisilane with this compound at 500–550°C led to the formation of the heterocyclic compounds (IX)–(XI) with an overall yield of about 45%. The addition of dichlorosilylene tentatively proceeds via the following mechanism:



IX

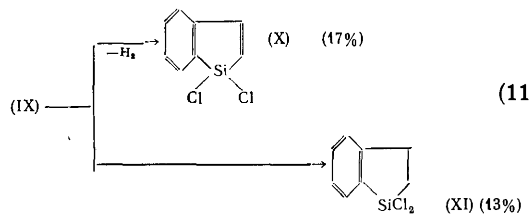
(111)

The isomerisation of the cyclo-octatetraene skeleton to the conjugated form (B) prior to the addition step is equally possible:



(A) (B)

1,1-Dichloro-8,9-dihydro-1-silaindene (IX) is fairly unstable at high temperatures and is dehydrogenated with formation of 1,1-dichloro-1-silaindene (X). The isomerisation of compound (IX) with formation of 1,1-dichloro-1-silaindan (XI) also proceeds to some extent:

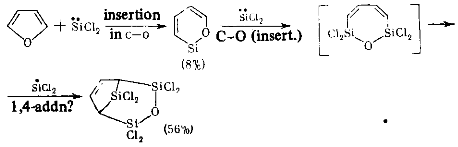


(112)

Benzene and its derivatives are known to be unreactive as trapping agents in relation to organic silylenes[2] and they should probably also exhibit a low reactivity in relation to other silylenes in the singlet state. Nevertheless one should note that biradical difluorosilylene polymers[216] as well as the less thoroughly investigated silicon monoxide react with aromatic hydrocarbons, forming cyclohexa-1,4-dienes[5,9]. The product of the reaction of silicon monoxide with benzene exhibits a high thermal stability[6].

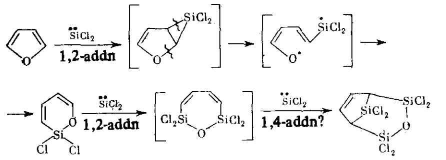
Reactions with Furan and Its Derivatives

The products of the gas-phase reaction of dichlorosilylenes with furan were unexpected[89-92]. The sequence of reaction steps can be represented in this instance by the following mechanism:



(113)

However, one cannot rule out another mechanism of the reaction, for example the addition of dichlorosilylene to the double bond of furan combined with a complex intramolecular rearrangement of the intermediate adduct:



(114)

The reaction with sylvan proceeds in the same way. The study of the interaction of perchloropolysilanes with this compound at 500–570°C showed that dichlorosilylene does not attack the methyl group; all the products detected were analogous to those isolated in the reaction with furan, the yield of the methyl-substituted bicyclic compound also being high (50%).

The examples discussed above demonstrate the enormous synthetic possibilities of the silicon analogues of carbenes (silylenes), the chemistry of which has been used in the solution of practical problems as a result of the efforts of many investigators. Summarising the foregoing, one may conclude that the chemistry of silylenes is in a state of vigorous development. This is demonstrated by the recent publications on the mechanism of the addition of phenylmethylsilylene to cyclohexene[277,278] and 2,3-dimethylbuta-1,3-diene[279] and of the addition of dimethylsilylene to cyclohexa-1,2-diene[280], which has provided evidence for the formation of intermediate silacyclopropanes. Methods for the generation of silylenes are also being improved, in particular the existing methods have been supplemented by a new procedure whereby dimethylsilylene is obtained under the mild conditions of the thermolysis of hexamethylsiliran, which until recently was completely inaccessible[281]. The above trends have been reflected also in certain recent publications[282-299], which appeared during the preparation of the review for the press. All these factors give rise to the hope for a rapid improvement of the existing methods for the synthesis and investigation of silylenes, which will undoubtedly help to predict, in a broad outline, the mode of reactions in systems which have not so far been investigated.

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† Potter's earlier studies are apparently to be found in the Patent literature.

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Some Aspects of the Theory of Gel Formation in Reactions of Polyfunctional Compounds

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Various theories of gel formation by three-dimensional polymers derived from polyfunctional monomeric and oligomeric compounds, ranging from the theory of Carothers and Flory to the modern theories of Gordon, Kilb, Frisch, Bruneau, and Stepto, are discussed. The role of kinetic, thermodynamic, and structural factors in processes leading to the development of the gel fraction are analysed. The reactions involving polyfunctional compounds are classified, and the fundamental scheme of the three-dimensional reaction leading to gel polymers is described taking into account the altered ideas and the new criteria which have been established. The conclusions reached at a symposium on gel formation processes in polymers held in England in 1974 are examined.
The bibliography includes 149 references.

CONTENTS

> ...The theory and its scope are at the
> half-way point between chemists,
> physical chemists, and biologists on
> the one hand, and mathematicians
> on the other.
> C.Bruneau, Am. Chim., 1, 271 (1966)

I. CLASSICAL CONCEPTS AND LAWS OF FUNCTIONALITY

The ability of a polymeric system to be converted irreversibly into an infusible and insoluble state, i.e. to promote gel formation[†], has been used for a long time in various branches of industry. It is not therefore surprising that, ever since the first steps were taken in polymer chemistry, numerous applied and theoretical studies have been devoted to the phenomenon of gel formation in three-dimensional polycondensation and polymerisation and to its interpretation and characteristics.

The role of the functionality of compounds (i.e. the number of functional groups per monomer molecule) was noted and analysed before all other factors exerting the most marked influence on the development of the gel formation process in polymers during three-dimensional polycondensation. In 1932 Bozza[1] characterised for the first time the dependence of the degree of reaction of Glyptal polymers, including the degree of condensation at the instant of gel formation (the gel formation point), as a function of the functionality of the system.

This study stimulated the development of ideas about gel formation in polymers. It had a definite influence on Carothers, who presented evidence in his 1935 paper "Polymers and Functionality"[2] that the dependence of the degree of reaction on functionality in gel formation by polymers is of a general type. Carothers' initial postulates (1) that the onset of gel formation is due to the formation of infinite three-dimensional (spatial) networks and (2) that the importance of the intramolecular cyclisation of the initial compounds is negligible determined for a long time, together with subsequent studies by Flory, a unilateral development of the theory of gel formation. Perhaps the most complete and at the same time briefest assessment of Carothers' "classical" ideas is given in the monograph of Cotter and Matzner[3]: "It is interesting to speculate whether Carothers' work, being so basic and all-encompassing, served to inhibit subsequent creativity in synthetic polymer chemistry. Frequently, when rapid, broad studies are made in a field of scientific endeavour, they can serve as unintentional barriers to further advances... The wide scope that is only now emerging for ring-forming polymerisations of polyfunctional monomers to linear polymers is indeed remarkable. Its appearance may well have been delayed by the functionality laws of polymer science".

The derivation of the system of Carothers' fundamental equations, subsequently called the "law of functionality", is based on a simplified analysis of the formation of a polymer molecule from N_0 monomer molecules with an arithmetical mean functionality f'. In the absence of intramolecular reactions, the combination of each two monomer molecules by a single covalent bond (i.e. as a result of the disappearance of two functional groups) corresponds to an overall decrease in the number of molecules equal to $2(N_0-N)$, where N is the number of molecules in the system after the attainment of a particular degree of reaction. Having referred the number of groups which have reacted to their initial number, Carothers arrives at the degree of conversion at any polycondensation stage before the attainment of the gel formation point:

$$P=2(N_0-N)/N_0f. \qquad (1)$$

[†] In the present review the terms "gel formation", "micro- and macro-gels", "the point of gel formation", "the theory of gel formation", "the gel formation period", "the sol fraction", etc. refer to the description of the formation of polymers with a three-dimensional macromolecular structure produced only as a result of covalent bonds on condensation or polymerisation of polyfunctional compounds.

Putting $N_0/N = X$ (the number-average degree of polymerisation), we obtain

$$P=2/f-2/Xf, \tag{2}$$

whence

$$X=\frac{1}{1-Pf/2}. \tag{3}$$

Assuming that $X = \infty$ at the gel formation point, Carothers defines the conversion at this point in the following way:

$$P_{cr}=2/f. \tag{4}$$

Analysis of the above equations shows that their application is rigorously limited by the following condition: none of the functional groups of the monomer or the polymer molecule is involved in the formation of any cyclic groups or fragments. The unreality of this condition was noted already in the course of the first discussion after Carothers' report on this subject. Using the model of a three-dimensional process illustrated in Fig. 1, Houwink[4] showed that Eqns. (1) and (2) are invalid. According to Houwink, when a polymer molecule A with functional groups X has reacted with another molecule B as a result of the interaction between groups *1* and *4*, then, following the further development of their process, for example on interaction between groups *2* and *5* or between groups *3* and *6*, there is no increase in the degree of polymerisation $X = N_0/N$, since the number of molecules N does not decrease. Consequently the degree of conversion actually increases, while according to Eqns. (1) and (2) it should have remained constant. Furthermore, Eqn. (3) loses its physical significance for conversions in excess of $2/f$, when the number-average degree of polymerisation becomes negative.

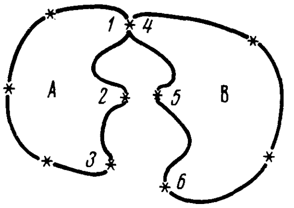


Figure 1. Houwink's model of the intramolecular cyclisation process[4].

Later it was shown[5] that the number-average degree of polymerisation at the gel formation point is extremely low, as a result of which Eqn. (4) is also contradictory.

The specific nature of the initial postulates of Carothers' theory has now also become evident. Various causes and mechanisms of gel formation in polymers, according to which the formation of an infinite three-dimensional macromolecular network is by no means a necessary criterion of this phenomenon, will be examined below. As regards the second postulate, neglect of intramolecular cyclisation processes in the macromolecular system was not only unjustified, as stated above, but actually became a definite obstacle to the development of theoretical ideas.

A more fundamental mathematical approach to the analysis of gel formation in polymers was achieved a few years later in Flory's studies[6-9], where the statistical theory of probability was first applied to three-dimensional polycondensation. It is striking that, like Carothers, Flory believes that the onset of gel formation is caused by the generation of "infinite" spatial polymeric structures. For the statistical analysis and derivation of fundamental relations, Flory employed the diagram describing the formation of a three-dimensional macromolecule illustrated in Fig. 2*a*. The same model has been frequently used by other investigators in the form of modifications 2*b* and 2*c*. Considering the probability that any chain selected at random from the polymer mixture, for example the chain in sphere *1* in Fig. 2*a*, is part of an infinite three-dimensional molecule, Flory bases his treatment on two hypotheses which he adopted *a priori*. The first is that all processes leading to the formation of cyclic groups or fragments are unlikely and are therefore disregarded. The second hypothesis is that all the reactive groups have the same reactivity throughout the process regardless of their position. Thus having placed at the head of his theory the same postulates as in Carothers' treatment, Flory actually examined one of the specific instances of three-dimensional polycondensation, namely the instance where only statistical relations and not chemical relations are dominant.

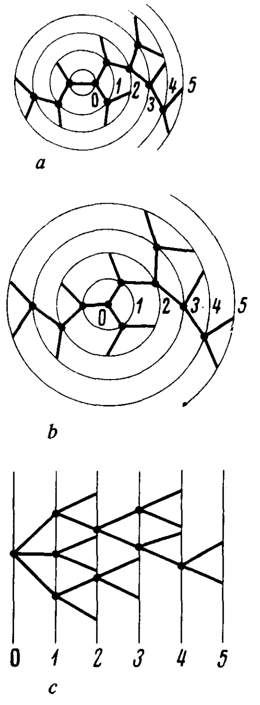


Figure 2. A topological scheme of the development of a three-dimensional polymerisation reaction: *a*) Flory's model[6]; *b*) the "growing tree" model[36]; *c*) the cascade process model[36]. The numerals represent the generations.

One of the most important parameters of Flory's theory is the branching coefficient α, which he defined as the probability that one branching component (the monomer with $f > 2$) becomes bound as a result of the reaction with another branching component. The author identified the onset of gel formation in polymers or the gel formation point with the critical conditions for explosion in certain gas-phase reactions, having shown that the overall critical value of α can be represented thus:

$$\alpha_{cr} = \frac{1}{f-1}, \tag{5}$$

where f is the arithmetical mean functionality of the branching components only [for example f for a mixture of two moles of glycerol, one mole of pentaerythritol, and give moles of dicarboxylic acid is $(2 \times 3 + 1 \times 4)/3 = 3.33$]. On the other hand, the statistical method leads to a dependence of α on the degree of condensation P:

$$\alpha = rP_A\rho/[1 - rP_A^2(1-\rho)] = P_B^2\rho/[r - P_B^2(1-\rho)], \tag{6}$$

where r is the ratio of the total number of groups A to the total number of groups B in the system, ρ is the ratio of the number of groups A belonging to polyfunctional monomers to the number of groups A in the system, and P_A and P_B are the degrees of conversion with respect to either groups A or B [Eqns.(5) and (6) were derived by Billmeyer[5]]. Evidently in the calculation of α_{cr} it is necessary to know only the functionality of the reactants. Using Eqn.(6), it is easy to calculate the degree of conversion in the reaction at the gel formation point of the polymers when α_{cr} is known.

It was found that Flory's theoretical ideas made it possible to describe the onset and development of gel formation in any polycondensation system without resorting to experiment. This appeared to be very promising, particularly from the standpoint of the practical application of the theory.

Table 1. The degree of conversion P, the branching coefficient α, and the functionality f in systems of polyfunctional monomers (according to Flory[6-9] and Carothers[2]).

Monomer system*	According to Flory			According to Carothers	
	f	α_{cr} from Eqn.(5)	P_{cr} from Eqn.(6)	f	P_{cr} from Eqn.(4)
$2A_3 + 3B_2$	3.00	0.50	70.71	2.40	83.33
$A_3 + B_3$	3.00	0.50	50.00	3.00	66.66
$A_4 + 2B_2$	4.00	0.33	57.73	2.66	75.00
$3A_4 + 4B_3$	3.42	0.41	41.17	3.42	58.33
$A_4 + B_4$	4.00	0.33	33.33	4.00	50.00

*The subscripts correspond to the number of groups per molecule.

Emphasising the generality of the relations obtained, Flory also noted that the conversion in the reaction at the gel formation point P_{cr} is independent of process conditions such as temperature, catalyst, reactant concentrations, etc.[6] Table 1 presents the characteristics, in terms of the Flory and Carothers theories, of a number of heterofunctional condensations in which the ratio of the interacting functional groups A, and B is 1 : 1, i.e. $r = 1$ in Eqn.(6). It follows from the data in Table 1 that the degree of conversion at the gel formation point, calculated from the Carothers theory, is greater than the value calculated from the Flory theory, which is due to the incorrect estimate of X in Eqn.(2), as a result of which the second term assumes a value close to zero and Eqn.(2) assumes the form of Eqn.(4).

Flory compared his theoretical treatment with the comparatively few available experimental data. The scant experimental material at that time and possibly also pure chance led to the adoption of polyesters as a practical model. Comparison shows (Table 2) that the discrepancies between theory and experiment are comparatively small, but exceed the permissible deviations in theoretical studies[6-9]. Although the author attributes the observed discrepancies to neglect of intramolecular cyclisation reactions in the calculations, he excludes them from the first phase of polycondensation (before the instant of the gel formation), evidently because they are inconvenient for mathematical treatment, and transfers them wholly to the second stage—beyond the gel formation point. This is illustrated by the course of the analysis itself and by the working scheme (Fig. 2). According to the initial postulate of the Flory theory, gel formation is a process involving the growth in the reaction mixture of giant macromolecules with a three-dimensional structure. The latter are none other than a statistical set of cyclic fragments linked in space. As can be seen from Fig. 2, Flory analyses the probability of the formation of an infinitely large branched (but not cross-linked) polymer, which suddently begins to undergo three-dimensional cyclisation only at the gel formation point, and not the probability of the formation of such polycyclic *macro-ensemble*.

Table 2. The experimental and calculated degrees of condensation and the branching coefficients at the gel formation point (according to Flory) for systems comprising tricarballylic acid, diethylene glycol, and dicarboxylic acids.

No. of expt.	P_{cr}		α_{cr}		No. of expt.	P_{cr}		α_{cr}	
	expt.	calc.	expt.	calc.		expt.	calc.	expt.	calc.
1	0.911	0.879	0.59	0.50	3	0.894	0.843	0.62	0.50
2	0.939	0.916	0.59	0.50	4	0.990	0.995	0.58	0.50

Stockmayer and Weil[10] subsequently attempted to test experimentally this artificial subdivision—into a polymer branching process alone in the first stage and mainly the formation of a three-dimensional macromolecular network structure in the second. In their attempts to refine the fundamental equations of the Flory theory, Stockmayer and Weil[10] and subsequently Weil[11] diluted the reaction mixtures with inert solvents. This method made it possible to take into account quantitatively the specific contribution of the intramolecular cyclisation reactions. Having determined the gel formation point in highly dilute mixed solutions of adipic acid and pentaerythritol, where intramolecular cyclisation should have played a significant role, Stockmayer subsequently proceeded to more concentrated solutions. Having observed that the graphical relation between P_{cr} and the volume of the reaction mixture is a straight line, he extrapolated it to zero volume and obtained values of P_{cr} in good agreement with those calculated by Eqn.(6).

Numerous cyclisation reactions of various monomers not only in dilute solutions but also in reaction media without solvents are now known[12]. In the light of the accumulated experience, the relation which Stockmayer obtained by extrapolation is characteristic of the given specific instance only.

Summarising the initial period of the establishment of a theory of gel formation in polymers, we may note that, as a result of the development of the first theoretical ideas based on the few experimental data available at the time, a number of characteristic relations, illustrated graphically in Figs. 3–5, became generally adopted in 1940 to 1945.

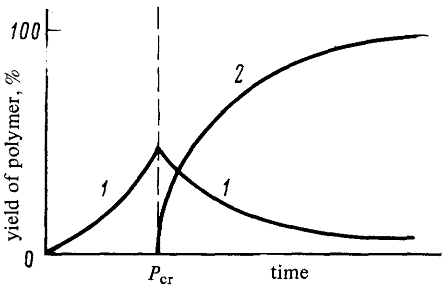


Figure 3. The yield of soluble polymeric products (curve *1*) and of the gel fraction (curve *2*) in the three-dimensional condensation of polyfunctional compounds.

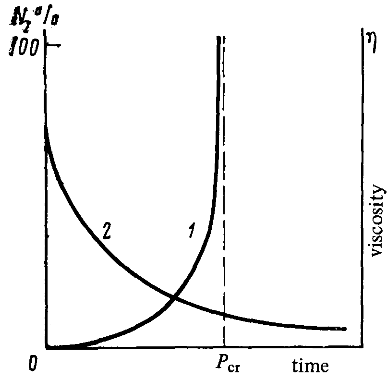


Figure 4. Variation of the viscosity of the products η (curve *1*) and of the content of functional groups in the system N (curve *2*) during condensation.

It follows from the graphs that the gel formation point of a polymer was adopted as the turning point in the reaction, dividing the process into two stages. The formation of oligomeric products is characteristic of the first stage. Their interaction with one another and with the initial monomers is responsible for the appearance of branched macromolecules, whose yield increases during the condensation, reaching a maximum at the gel formation point (Fig. 3, curve *1*). A gradual decrease of the sol fraction because of the involvement of the polymer molecules in the formation of the spatial network, i.e. the increase of the content of the gel fraction in the reaction system, is characteristic of the second stage of the condensation (Fig. 3, curve *2*).

It follows from the data in Fig. 4 that only a slight increase of the viscosity of the products is typical for the first reaction stage, but, as the reaction approaches the gel formation point, the tendency towards a sharp rise in the kinetic viscosity curve is observed (curve *1*). Diffusional factors play an increasing role at this stage and the curve describing the consumption of functional groups becomes less steep and approaches an asymptote (curve *2*).

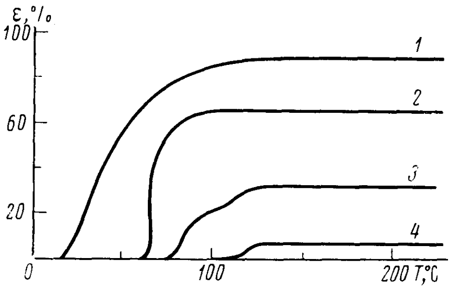


Figure 5. Variation of the thermomechanical properties of polymers beyond the gel formation point with increase of the density of cross links (a higher number of the curve corresponds to a higher density of cross links); ϵ—modulus of elasticity.

Beyond the gel formation point, it is more difficult to follow the conversion in the reaction on the basis of the content of functional groups. However, the change of the physicomechanical characteristics of the gel fraction makes it possible to infer a further development of the process. Thus an increase of the modulus of elasticity and an increase of the glass point (Fig. 5) as well as changes in other characteristics correspond to an increase of the density of cross links in the growing network owing to the continuing polycondensation within the gel particles. However, even for high degrees of conversion of the polymeric system into a gel, it is possible to extract from the latter a soluble fraction (the sol fraction), the molecular weight of which is low.

The above mechanism of the three-dimensional polymer formation process, whose arose as a result of the period of "classical" studies and ideas, was used subsequently by many investigators as the fundamental model. The main component of this model, the gel formation theory, was elaborated and adjusted. However, as long as the ideas and postulates underlying it remained unchanged, further progress was bound to be limited.

II. THE ROLE OF APPLIED MATHEMATICAL METHODS IN THE FURTHER DEVELOPMENT OF THE THEORY

A characteristic feature of the subsequent development of the theory was a comprehensive analysis of the known relations governing the process in conjunction with various mathematical methods. The mathematical procedures and approaches would merit only a simple enumeration if they did not reveal at the same time "latent" relations and characteristics in the formation of macromolecules with a three-dimensional structure, demonstrating thereby the primitive nature of the "classical" gel formation mechanism as well as the importance of a wide variety of factors which had been neglected previously.

In the course of the study of the mathematical models of three-dimensional polycondensation, the complexity and many-sided nature of this process, the role of the activity of functional groups and their distribution in the molecule, the importance of various characteristic macrochains, the structural forms of oligomers and polymers, etc., became increasingly clear. At the same time there was a growth of the complexity of the mathematical expressions describing particular characteristics.

However, instead of carrying out specific chemical tests of the relations obtained, investigators moved further into the region of purely mathematical manipulations. Thus Flory[6] described gel formation in terms of the model of a branching process (based on Semenov's theory[13] developed in the 1930s and describing the critical conditions in the explosion in certain gas-phase reactions) in combination with a statistical method of calculation. Stockmayer employed another analytical method[15-17] adopted from the theory of non-ideal gases[14]. Applying this method, he used the analogy between the phase transition from gases to liquids and the transition from the liquid soluble polymer at the gel formation point to the insoluble and infusible macrogel. The method yielded more general expressions for the fundamental characteristics of three-dimensional processes and made it possible to consider cases which Flory was unable to solve[15-17]. In particular, Stockmayer analysed the copolymerisation of vinyl and divinyl monomers, requiring a special approach, and found a general expression for the description of the "critical state" of the system. He also attempted to take into account the erroneous assumptions of the "classical" theory, namely to determine the contribution of the processes involving the formation of cyclic fragments in the molecular chains before the gel formation point[10].

Gordon[18] and Good[19,20], who applied the methods used for the description of cascade processes[21,22], found a greater scope for the mathematical analysis of polymerisation processes. The cascade theory or the theory of stochastic processes was a more advanced and convenient instrument compared with previous theories. The relation which Good found between the number-average degree of polymerisation DQ_w and the branching coefficient α has the following simple form:

$$DQ_w = \frac{4-\alpha-\sqrt{4\alpha-3\alpha^2}}{3\alpha-4+3\sqrt{4\alpha-3\alpha^2}}.$$

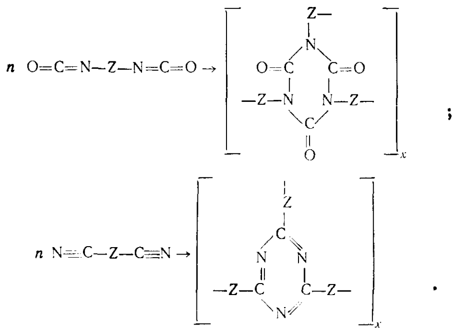
Furthermore, Good tabulated the calculated values of DQ and α for monomer systems with a tetrafunctional branching unit.

Thus the studies of Gordon and Good permitted an advance in the methods of mathematical analysis in this field. The cascade method was developed further a few years later in Whittle's studies[23,24]. Having examined the problems of the formation of bonds between reacting species with functional groups having different reactivities as well as the probability of their aggregation, Whittle extended the analytical method to more realistic but also more complex cases of the aggregation of macromolecular species with groups having different reactivities. His mathematical expressions were not, unfortunately, sufficiently simple and complete for practical applications.

Studies by Case[25-28] and Giacomo[29] played a major role in the progress in the physicochemical description of the gel formation process. Bearing in mind the primitive nature of Flory's mechanical model of the monomer, as an indefinite particle with functional groups, these workers took the first step on the way to the analysis of a monomer model with a definite structure, attempting to take into account the influence of the symmetry of the disposition of the functional groups in the molecule. This was the first attempt at a mathematical approach to the true behaviour of real compounds in three-dimensional processes. Despite the fact that Giacomo and Case took into account only one of the numerous characteristics of monomeric compounds influencing the gel formation process, namely the asymmetry of the distribution of the functional groups in the molecule manifesting different reactivities, they noted significant differences in the behaviour of these more realistic models compared with Flory's model.

Improvement of the mathematical procedures in the analysis of three-dimensional polycondensation led in its turn to the consideration of more complex and realistic models. Erlander and Fench[30], Tang Au-Chin[31], and Allen[32] achieved a mathematical description of the three-dimensional polycondensation of monomers whose molecules contain various functional groups or identical groups with different reactivities.

The studies of Fukui and Yamabe[33-35], devoted to the mathematical analysis and description of at first sight seemingly highly specific instances of three-dimensional processes, were published in 1960–1964. In the development of the synthesis of thermoreactive resins, the authors considered and analysed the formation of a three-dimensional polymer from polyisocyanates, polynitriles, and certain other monomers:



Apart from the isocyanuric and triazine cyclic *macroensembles* illustrated above, the polycyclic hexadihydrotriazine, boron oxide, and other polymers have similar structures.

It follows from the reaction equations that a branched cyclic structure is formed from the very beginning in such processes, and is converted in the course of further development into a three-dimensional structure. The formation of rings is the main process in this case and must be described by the main equation and not with the aid of average corrections, as has been done previously by Stockmayer, Case, and others. Using the old statistical methods, Fukui and Yamabe arrived at an expression describing the critical state in such systems:

$$\alpha_{cr} = \frac{1}{2(f-1)}.$$

Unfortunately due attention was not subsequently devoted to the mathematical analysis of polycondensation occurring with simultaneous and regular cyclisation and branching in the macromolecular chains.

The specific features of the formation of various chemical bonds, intermolecular and intramolecular, as well as the characteristics of the macromolecular structure generated were analysed some years later by Bruneau[36-40]. His studies were, as it were, a logical continuation, but at a higher mathematical level, of the research of Fukui and Yamabe. Bruneau examined the changes in a polyfunctional system during the reaction from two standpoints—structural and stochastic. The structural or topological aspect revealed an *ensemble* of the possible conformations of the intermediate products in the form of a Konig graph[41], while the stochastic approach made it possible to describe the chemical reaction at each instant in the form of a statistical distribution of the chemical bonds formed between the reactive molecule. The stochastic analysis led to the isolation of two types of systems of polyfunctional compounds, the real existence of which is evident: (1) the homogamous system in which a bond is formed between any pair of species (molecules) and (2) the heterogamous system where chemical bonds are formed in a specific manner. Bruneau did not insist categorically on the universality of the relations obtained, bearing in mind apparently the wide variety of factors which are difficult to take into account and which have different effects (depending on the type of reactants) on the critical parameters of gel formation. In concluding one of his communications[40], he emphasises that one can determine with the aid of his equations the critical parameters of gel formation only subject to the condition "that the mechanism of the reaction of polyfunctional monomers is known, that the formation of the three-dimensional structure satisfies the conditions of the theoretical method, and that the technique of the determination of the sol-gel transition is sufficiently sensitive and accurate".

Claiming that the gel formation theory is at the half-wave point between physics, chemistry, and biology, on the one hand, and mathematics, on the other, the author[36] endeavoured to demonstrate to workers in the former field the importance of the graph theory in the determination of the statistical structure of macromolecular compounds and to stimulate workers in the latter field to turn their attention to a particular branch of chemistry, with its topological possibilities in the study of the structure of polymers, which is exceptionally important in practice.

Apart from the above aspects of the study of the phenomena of gel formation by means of various mathematical approaches, it is also necessary to consider specifically the kinetic method of treating the problem. A number of workers supporting the kinetic approach in this field believe that the foundations of the statistical methods have been by no means adequately investigated and that this precludes *a priori* inferences about the possibility of applying it to calculations on processes of any specific type[42,43]. In contrast to the statistical method, based on the determination of the probability of the formation of macromolecules of a particular size and structure, the kinetic analytical method makes it possible to discover relatively general procedures for the calculation of the fundamental statistical characteristics of the distribution and to establish relations which determine the conditions governing the onset of gel formation in polymers.

Gordon and Scantlebury[44], who, among others, pioneered the kinetic approach to the study of gel formation in polyfunctional systems, used the statistical kinetic method to describe the condensation of adipic acid with pentaerythritol and tri(hydroxymethyl)ethane. In their assessment of the non-kinetic Whittle[23,24] and Bruneau[36] methods, these authors describe them as highly unrealistic statistical procedures, because they are not based on configuration statistics. Gordon and Scantlebury justified the proposed model for the gel formation process by solving equations involving functions of the ratio of carboxy- and hydroxy-groups. They found that at the beginning of gel formation about 10% of all the ester linkages formed are intramolecular. Such a high percentage contribution of the intramolecular cyclisation reactions threw doubt on the validity of models of the Carothers–Flory type (see Fig. 2), although the authors themselves did not discuss problems of this kind.

A very detailed mathematical description of the kinetics of the condensation of polyfunctional monomers was achieved recently by Pis'men and Kuchanov[42,45,46]. Using the reaction of glycerol with dicarboxylic acids as an example, they carried out calculations on the kinetics of the polycondensation of monomers containing reaction centres of different activities and obtained an analytical solution to the kinetic equation relating the molecular weight distribution of the products in the general case. These investigators also proposed for aromatic monomers a kinetic polycondensation mechanism in which the activity of the functional groups changes in the course of the reaction and showed that such instances cannot be described by a statistical method. The solution of the differential equations proposed[42] for the generating functions is, however, fairly difficult in most cases[47]. The application of this type of method to the description of condensation is further limited by the instant of gel formation.

In order to simplify the kinetic analytical method and the final equation, Irzhak[47] proposed a combinatorial method combining the familiar procedures and the criteria of the statistical method. In those cases where the detailed mechanism of the condensation process is known, he introduces the time characteristics of the reaction taking place. However, together with the statistical approach, the author introduced into his treatment the earlier assumptions of the statistical theory.

Summarising in 1968 the progress achieved in the mathematical description of polymerisation processes accompanied by gel formation, Gordon and Scantlebury noted[48] in the first place the importance of employing kinetic factors in the analysis (including the so called substitution effect[49], which determines the change in the rate of formation or dissociation of bonds during the reaction) and, in the second place, the greater attention paid by mathematicians to the problem of intramolecular cyclisation[50-52]. The analytical description of this simultaneous process still constitutes an unsolved problem[43,56], despite the continuing elaboration of the method[53-55].

In connection with the improvement of the mathematical procedures for the analysis, one can also expect much interest in other secondary reactions, which are no less important than intramolecular cyclisation. The influence of secondary reactions on the fundamental gel formation parameters and the properties of polymers has been frequently noted for many known classes of polymers[57]. The role of such processes is particularly important in the synthesis of elastomers[58], where the contribution of secondary reactions depends to a large extent on the conditions and increases with the degree of conversion of the monomer. One of the simplest cases of the analysis of secondary reactions—chain termination in the development of three-dimensional structure—has been examined in a study[59] where use was made of the theory of branching processes[18-21]. The mathematical description of three-dimensional polycondensation with simultaneous allowance for at least two similar factors, for example of chain transfer and cyclisation reactions, has not so far been achieved.

The characteristics of the development of the sol fraction in structured systems still require a mathematical treatment; certain variants of the analysis of its formation in conjunction with the series of assumptions and simplifications used previously have been examined[60-63]. The models of the development of the sol fraction in the studies quoted above differed little or not at all from the models proposed previously by Carothers[2] and Flory[6-9] (Fig. 2). For this reason, the studies concerned with the statistical mechanics of polymers with the star structure[64-66] adjoin this field in the mathematical analysis of three-dimensional processes.

The updating of the mathematical procedures for the investigation of three-dimensional polycondensation together with the development of synthetic methods had a further positive aspect, namely it helped to discover the error of certain assumptions and the final equations of the statistical method forming part of the procedures inherited from the 1930s. Andrianov and Emel'yanov[67,68], Pis'men and Kuchanov[42], and Raspopova et al.[43] showed that the logical and mathematical errors have been caused by the invalid application of certain procedures of the statistical method, which are in essence inapplicable to the description of chemical processes of this kind.

The latter may be illustrated by the studies of Bruneau[38,39] and certain other investigators[69-73] who demonstrated the formal contradictions arising from the "classical" theory of gel formation in a system of polyfunctional compounds. Whiteway et al.[69-71] noted with astonishment that the errors made by Flory in his first studies dealing with three-dimensional polycondensation have been frequently repeated by other investigators in the course of several decades.

III. THE GEL FRACTION AND DEVELOPMENT OF THE STRUCTURAL AND THERMODYNAMIC ASPECTS OF THE GEL FORMATION THEORY

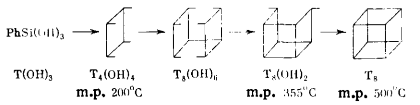
The concept of the "gel formation point" in a system of reacting polyfunctional compounds as the instant of the appearance in the reaction mixture of infinite polymeric three-dimensional structural networks (more correctly networks bounded by the walls of the reaction apparatus) was first introduced by Carothers[74] in 1931. Several years later, Staudinger[75-77] and then Flory[6] completed the formulation by defining a necessary condition for gel formation—the infinite growth of macromolecules in three directions. Thus, at the start of the development of polymer chemistry, three of the greatest authorities closely related the concept of the "gel" or the gel fraction to two factors: (1) the three-dimensional or spatial structure of macromolecules and (2) the "infinite" molecular weight.

Whereas the structural factor, which determines the most characteristic properties of the gel formation—its infusibility and insolubility in all solvents (not causing the dissociation of covalent linkages)—has not so far aroused any doubts, it was subsequently discovered that the necessity for the second factor does not by any means apply to all types of three-dimensional polymers.

The obligatory requirement of the formation of infinitely large gel macromolecules, in fact of a single macromolecule, was justified initially by the idea that a three-dimensional gel can be formed either by the cross-linking of macromolecules with a linear structure formed beforehand or via the family tree [multifunctional branching] mechanism proposed by Flory[6] (Fig. 2). Polymeric gels synthesised in accordance with the first variant did indeed correspond to all the factors mentioned above. This pathway is characteristic of the synthesis of elastomers and rubbers—polymeric materials subjected to some type of treatment in the last stage of their synthesis, for example by irradiation. A mathematical analysis of polymer-analogue reactions of this kind has been carried out by a number of investigators[78-81].

The ideas concerning the development of the process via the family tree mechanism with conversion of the branched macromolecules at the gel formation point into a three-dimensionally cross-linked polymer changed appreciably following the accumulation of experimental data. These changes were a consequence of advances in the synthetic methods of polymer chemistry and were determined primarily by the development of ideas concerning the three-dimensional processes proceeding via the microgel formation stage.

Despite the fact that studies devoted to the "embryonic" development of microgel molecules in processes of the above type are at present in the initial stage of their development, fairly thoroughly investigated pathways to the synthesis of a number of polycyclic homologues, which to a certain extent can serve as a model of developing three-dimensional structures, have already been described in the chemistry of polyorganosiloxanes for example. Thus the homocondensation of trihydroxyphenylsilane yields, apart from other polycyclophenylsiloxanes[82], a series of molecules with increasingly complex structures[83,84] (T denotes the trifunctional phenylsiloxane unit):

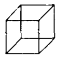


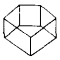
In the series of homologues illustrated, the solubility decreases and the melting point increases as the three-dimensional structure is formed and becomes more complex.

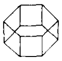
The influence of factors such as the flexibility of the molecular chain between the units of the polymer network on the capacity of the system for gel formation has been investigated in a number of studies by Andrianov and Emel'yanov[85-88] in relation to the three-dimensional polycondensation of tetrafunctional acid esters with tri- and tetra-hydric alcohols, various glycols, and diamines. The gel formation parameters determined in the reaction of oligomeric compounds (the critical degree of reaction and the critical branching coefficient) showed that, with increase of the length of the chain between the units of the polymer network, the instant of the appearance of the gel fraction is displaced towards increasing degrees of reaction, i.e. in the direction of the formation of more complex molecular structures. A similar relation was observed with increase of the flexibility of the chains between the units of the polymer network owing to another factor—the chemical nature of the macromolecules[67,68].

Among other structural factors directly responsible for the onset of the development of gel formation, the appearance of an additional number of units in the polymer network owing to the intertwining of the chains (entanglement) is important[89]. Despite the complexity of the analysis of this type of problem, the formation of hooking units can be followed, for example, by analogy with the method of Gartsman and Gorelik[90] or other workers[91].

A characteristic feature of molecules with a three-dimensional structure, namely the dependence of the melting point on the flexibity (elasticity) of the three-dimensional skeleton, has been traced also in another homologous series (polyphenylsilsesquioxanes)[84]:


T_8, mol. wt.1052
m.p. 500°C


T_{10}, mol. wt.1290
m.p. 418°C


T_{12}, mol. wt.1548
m.p. 385°C

Here the melting point decreases from T_8 to T_{12}, i.e. with increase of the elasticity of the lattice owing to the increase of the dimensions of the component rings.

Despite the logical incompleteness of the homologous series illustrated (the lack of the simplest model species which is built up to give a more complex three-dimensional lattice and which loses in this process both its fusibility and solubility in all solvents), certain purely structural characteristics can be traced in these instances: (1) the increase in the complexity of the molecular structure of the product during the reaction from dimeric to trimeric with its subsequent development is responsible for the gradual loss of solubility by the reaction products and for the increase of the melting point. (2) The loosening of the three-dimensional structure, i.e. the decrease of the number of bonds per unit volume and the consequent increase of the flexibility of the lattice, leads to the reverse effect—the increase of the solubility of such macromolecules and the decrease of their melting point.

In their study on the development of a theory of gel formation in the chemistry of alkyd resins, Bobalek et al.[92] proposed in 1964 a model for the process different from that of Flory (Fig. 6). This model differed in the first place by the fact that it actually altered the earlier concept of the gel formation point as the "critical instant resembling explosion in certain gas-phase reactions". It follows from Fig. 6 that the author distinguished two gel formation points. The first corresponds theoretically to the instant of the appearance in the reaction mixture of the first particles with a three-dimensional structure characterised by infusibility and insolubility. At this moment, the system is virtually homogeneous (there are only a few macromolecules with a three-dimensional structure) and, according to classical ideas, is not in a critical state. The second gel formation point corresponds to a much later reaction stage—the conversion of the fluid reaction mixture into an elastic polymer. In the author's terminology, this "physical" instant of gel formation is identical in terms of some of its characteristics to the established concept of the "classical" gel formation point (the loss of fluidity, fusibility, and solubility), but at the same time it exhibits fundamental differences—the gel particles appear and develop in the reaction mixture much earlier. Thus the hitherto clear-cut term "gel formation point" was transformed into the indefinite "gel formation period".

Studies by the Soviet polymer school later demonstrated, in relation to polyurethanes, the desirability of replacing the concept of the "gel formation point" by the more realistic "gel formation region"[93]. Electron microscope, molecular weight, and molecular probe studies by Lipatova, Lipatov, Zubko, and others in the course of the formation of polyurethanes with a three-dimensional structure[94-99] made it possible to demonstrate the appearance, already in the early stages, of globular formations with a greater or lesser degree of order in the supermolecular structures as a function of the number and positions of hydrogen bonds, the length and chemical nature of the chain in the initial compound, the reaction coditions, etc. The development of gel formation has then the properties of interglobular cross-linking and cross-linking within the globular structures. The two processes are interrelated and each may be dominant under certain conditions. The formation of the first sections of the microgel in the early stages does not in fact have any appreciable influence on the properties of the system (the latter remains fusible and fluid) but, as the microgel particles accumulate, there is a gradual transition from homogeneous to microheterogeneous conditions and then to macroheterogeneous conditions[100].

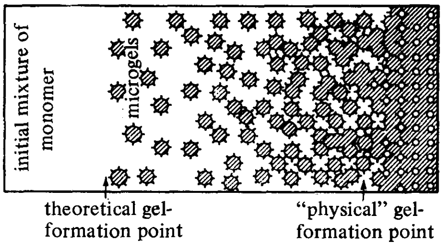


Figure 6. Schematic illustration of the formation of Glyptal polymers according to Bobalek et al.[92]

As in the study of Bobalek et al.[92] quoted above, two gel formation periods may be distinguished in the formation of polyurethanes. In the first stage network microgel particles are generated and their number increases. In the next stage, the main process involves the ~~linking~~ of the microgel particles as a result of which the system loses its fluidity and fusibility[98]. The indeterminate and diffuse nature of the boundaries of individual stages (homogeneity–microheterogeneity and microheterogeneity–macroheterogeneity) did indeed expand the "classical" definition of the gel formation point to the gel formation region or period.

The tendency to study the problems of gel formation in a number of investigations during 1960–1970[101,102] promoted a more detailed description of polymerisation processes, including transitional stages in microheterogeneous states. There was an increase in the publication of experimental data in the periodical literature, showing that macromolecules, oligomers, or monomers do not exist in an isolated state even in dilute solutions. According to the investigations of Lipatova and Proshlyakova[103], Kargin, Fakirov, and Bakeev[104,105], as well as other workers[106], the primary associated species, in the form of packets or aggregates combined in definite supermolecular structures, constitute the initial forms of the future microgel particles[107]. The involvement of the microgel particle formation stage in the three-dimensional processes was demstrated during these years for various types of polymers: polyacrylates[107-108], polyesters[92,109], polyurethanes[93-100], polyepoxides[110,111], etc. Ultimately it became evident that the specific contribution of the three-dimensional processes leading to spatial polymers via the microgel formation stage is no less significant than the contribution of the three-dimensional processes involving the formation of linear and branched macromolecular structures. In this sense, the model of a three-dimensional process proposed by Bobalek et al. becomes general.

The new mechanism has not been examined theoeretically in conjunction with a mathematical description.

The application of various physical methods to the study of three-dimensional reactions at the stages corresponding to the transition from homogeneous to microheterogeneous conditions made it possible to determine in many instances the size of the microgel particles[93,109,110].

The radius of the average globular formations in structured polyurethanes varies between 85 and 500 Å according to Lipatova's data[93]. With decrease of the molecular weight of the initial oligomer or with increase of the reaction temperature, the size of the nuclear gel particles then decreases, other conditions being equal.

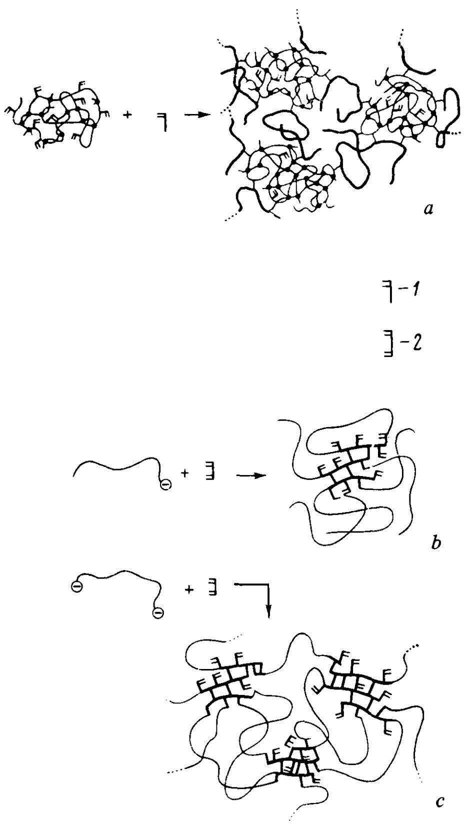
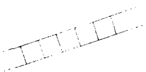
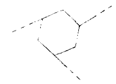
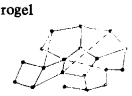


Figure 7. Schematic illustration of the directed "microgel" synthesis of three-dimensional polymers according to Funke[112] and Rempp[113]: *a*) reaction with participation of the microgel as the cross-linking agent in a three-dimensional process; *b*) synthesis of a polymer with a "star" structure containing a microgel nucleus; *c*) synthesis of a three-dimensional polymer with a porous structure; 1) vinyl monomer; 2) divinyl monomer.

Then, depending on the nature and properties of the microgel particles formed (the density of cross-linking within the microgel, the size and shape of the particle, the number of functional groups on the surface, etc.), the final product of the three-dimensional reaction is characterised to some extent by the inhomogeneity of its supermolecular structure. According to Funke[112], the homogeneity of the supermolecular structure of cross-linked polymers is an exception rather than the rule; on the other hand, the inhomogeneity of the structure of polymers can be regulated during the synthesis and it can assume organised forms. In his study of the general cases of the synthesis of three-dimensional polymers with inhomogeneous supermolecular structure, Funke put forward fundamental schemes for the synthesis of products with a predetermined structural heterogeneity (Fig. 7). It follows from Fig. 7*a* that the particles of the microgel formed beforehand can play the role of polyfunctional centres (cross-linking via the functional groups on the surface of the microgel), while the formation of linear chains between the centres can be achieved by the polymerisation of monovinyl compounds. Using the divinyl monomer and "live" poly(methyl methacrylate) chains, it is possible to synthesise either a polymer with a dense microgel nucleus and long side branches (Fig. 7*b*) or a cross-linked polymer with a supermolecular structure of a different type (Fig. 7*c*).[113]

Table 3. The development and products of polymerisation processes involving polyfunctional monomers.

Type of reaction	Development of reaction	Reaction products	References
I. Linear polycylisation	Two-dimensional development	Macromolecules with ladder or cycloladder structures	3,12,114, 117,119
II. Cyclotrimerisation with branching	Three-dimensional development of a polycyclic structure	 	
III. Branching with three-dimensional cyclisation		Macrogel Soluble and fusible branched polymer containing two-dimensional and three-dimensional cyclic products	33-35 82-84,53 118,125
	(a) Simultaneous competing branching and cyclisation reactions with the latter predominating;	See scheme in Section III Microgel 	112,115, 116
	(b) analogous process under associative conditions;		
	(c) statistical mean development of the same processes	Macrogel (with or without preliminary microgel formation) (see Fig.6)	92-100

The new trends in the synthesis of polymers, which developed as a result of the study and utilisation of polycyclisation reactions[3,12], altered radically the concept of the functionality of the monomer as the sole factor determining the possibility or impossibility of gel formation in polymers. To illustrate this fact, it is sufficient to compare Carothers' "law of functionality"[2,74] (the monomer system is incapable of forming a three-dimensional structure for $f \leq 2$ and a three-dimensional macrogel is necessarily formed for $f > 2$) with the development of only three types of polymerisation reactions, where the average functionality of the initial monomer mixture is $f > 2$ (Table 3).

The data in Table 3 show that the range of polymerisation processes in which polyfunctional compounds are used is limited, on the one hand, by reaction of type I and IIIa leading to soluble and fusible linear and polycyclic compounds and, on the other hand, by reactions responsible for the formation of three-dimensional macrogel products (type IIIc). Within the limits of this range, one can evidently expect a wide variety of combinations of the above types.

The role and importance of various factors in the development of gel formation in systems with a high functionality have been investigated in two-, three-, and six-component mixtures of organosilicon monomers. The results showed that, under certain conditions, the reaction can be directed towards the formation of soluble polycyclic systems. Such directing factors may be the nature of the solvent[118], the nature of the organic group[120], the pH of the medium[121], and others[122].

The high functionality of the initial compound thus frequently cannot serve as a criterion of the capacity of the system for the formation of three-dimensional polymers. Furthermore, when a polyfunctional monomer exhibits an enhanced tendency towards cyclisation, an increase in the tendency of the reaction products towards the formation of polymers with a three-dimensional macromolecular structure can be achieved by reducing the overall functionality of the system. In the manufacture of organosilicon polymers, an analogous operation is achieved in the synthesis of varnish and enamel binders of type KO (the introduction of a bifunctional compound into the reaction with a trifunctional compound). Characteristics of a similar type have been investigated in relation to the condensation of a tetrafunctional monomer whose capacity for the formation of three-dimensional structures appeared only following a decrease of the overall functionality of the system as a result of the introduction of a bifunctional compound, which interferes with the intramolecular cyclisation process[123]. Similar phenomena were observed also in multicomponent systems with a high average functionality[124].

Secondary processes such as rearrangement or chain-transfer reactions can also play a decisive role in controlling the development of the three-dimensional process. Thus, in a study of the polymerisation of bicyclic siloxanes ($f = 4$), Andrianov and Zachernyuk[125] established that, under certain conditions, the yield of the three-dimensional polymer passes through a maximum and then begins to decrease owing to the increasing importance of the rearrangement process, leading ultimately to completely soluble polycyclic systems.

The probability, degree, and causes of cyclisation in three-dimensional polymerisation processes constituted an urgent problem for both mathematicians and physical chemists from the very beginning of the theory of gel formation. As the problem became more complex and many-sided, the approaches to its solution also altered. The updating of the analysis of cyclisation proceeded along these lines gradually from the study of the influence of the dilution effect[11,51,52] to the study of the conformational statistics[36,116] of polymeric and oligomeric molecules and the discovery of more general relations.

Various methods have been proposed in recent years for the quantitative estimation of the degree of polycyclisation. A number of studies by Karyakin and coworkers[126-128] were characterised by attempts at a thermodynamic approach to the analysis of polyheterocyclic polymers with a linear structure, while kinetic solutions of problems of this kind were considered by Jacobson and coworkers[129,130]. However, the above analytical procedures were far from being universal[56].

The study and description of the laws governing the formation and development of three-dimensional cyclic structures, resembling, for example, the cubic polyphenylsilsesquioxanes, microgel structures of different types, and the conversion of the latter into macrogel forms undoubtedly constitute an even more difficult problem.

Thermodynamic and kinetic factors have evidently played a decisive role in the general characteristics of the properties of structured systems. In the kinetic and thermodynamic interpretation of gel formation in a system of polyfunctional monomers, two tendencies have been noted. The characteristic feature of one tendency is analysis of the early stages of the process[43,93,115,116]: (1) of the generation of a swarm of complexes and globular aggregates via physical interaction forces; (2) of intraglobular processes before the appearance of the first microgel particles; (3) of the conditions and causes of macro- and micro-gel formation. In terms of the mechanism of Bobalek and coworkers (see Fig. 6), these studies include the stage of the three-dimensional process up to and including the theoretical gel formation point.

The principal aim in the second trend is to study the relations governing the syneresis phenomenon in the polymer–solvent system, i.e. the phenomenon of the separation of the gel and sol fractions. The region beyond the theoretical gel formation point in Fig. 6, including the instant of "physical gel formation" (syneresis), corresponds to studies of this kind[109,131-135].

In the study of the development of the three-dimensional process in polyurethane systems, one of the principal causes of the involvement of the microgel formation stage in the reaction—the large energy of the intermolecular interactions in the initial system of components—was discovered[93]. In the assessment of the vigorous intramolecular cyclisation reaction in the synthesis of three-dimensional polymers, a number of investigators suggested that the cause of the anomalous process be sought by abandoning the model of intertwined macromolecular coils in solution[43,115].

In the course of the conformational analysis of polymer chains in concentrated systems, it was shown that the free energy of the system is determined not only by the free energy of the given chain but depends also on the nature and energetic state of other macrochains in the system. According to the results obtained, the fixation of the conformation of the molecules via physical forces in the first stage of the interaction is then completed by the cyclisation reaction occurring within a much more tightly coiled polymer compared with the θ-conformation and leading to a large number of cross links within the microgel particle.

A series of studies by Dusek[131-135] were devoted in recent years to the thermodynamic investigation of syneresis in three-dimensional processes. The author's approach to the analysis of the phenomenon is characterised by a distinction being drawn as a function of the type of conversion into a three-dimensional structure, which proceeds either via microgel or macrogel formation[131]. Assuming the employment of a solvent (or the initial monomer as the reaction solvent) to be the cause of the thermodynamic instability of the system during the reaction and also the cause of the inhomogeneity of the final polymer, Dusek calculated two critical parameters of syneresis. He considered a system of polymers where syneresis is determined by the increasing density of cross-linking in the macromolecule and the gel and sol fractions are separated after the attainment of the critical number of cross links ν per unit volume of the gel. In this case, when the separation of the system is due to polymer–solvent interaction forces, syneresis occurs following the breakdown of equilibrium and the attainment of the critical value by the interaction parameter χ. A combination of critical conditions with respect to ν and χ is evidently characteristic of the majority of three-dimensional processes. For the simplest version of a binary system, a formula has been found, whose solution leads to the determination of the parameters, i.e.

$$(\Delta\mu_i)_{\text{mix}} + (\Delta\mu_i)_{\text{network}} = \ln(1-\Phi_p^0) + \Phi_p^0 + \chi(\Phi_p^0)^2 + \nu\bar{V}\Phi_p^0/2 = 0,$$

where μ_i is the chemical potential of a given component in the mixture or in the three-dimensional network, Φ_p^0 the degree of swelling of the three-dimensional product in the given solvent, and $\bar{V}$ the partial molar volume of the solvent.

Evidently, among the multiplicity of objective factors responsible for the syneresis of the system, account was actually taken of only three and the observed relation governing the syneresis conditions in a polymer system constitutes therefore a convenient mathematical model rather than a universal equation. In an experimental test of the equation, a satisfactory agreement of the observed and calculated values was noted in the case of macro-syneresis. The calculations on microgel formation processes agreed with experiment less satisfactorily.

The state of the theory of gel formation in polymers and its present problems were considered at the April 1974 symposium in England devoted to gel formation processes and gels of all four types as defined by Flory[136]. The greatest attention in studies concerned with the formation of covalently linked three-dimensional polymer networks was devoted to the problems of inter- and intramolecular reactions, the aim being to create a single general theory.

In our view, Flory's introductory report[136] constituted a disturbing factor in this respect. Together with the likely usefulness of the statistical method in the theory of gel formation, he emphasised the legitimacy of arbitrary assumptions concerning the insignificant contribution of cyclisation reactions and the constancy of the reactivity of the functional groups in the course of condensation, i.e. the assumptions introduced into the analysis of gel formation as early as the 1930s.

The possibility of the development of the three-dimensional polycondensation process virtually without cyclisation up to the gel formation point, i.e. the possibility that the reaction proceeds via the family tree mechanism, was examined by Peniche-Covas et al.[137] in relation to the system of decamethylene glycol and benzenetriacetic acid. However, the only fundamental argument quoted by the authors in support of the cascade mechanism of the development of the reaction is the possibility of highly efficient extraction of strongly branched macromolecules with molecular weights up to 10^8 from the polymer system beyond the gel formation point (the system contained between 1 and 5% of the gel fraction). They did not confirm experimentally their conclusion that the "newly generated" gel should be virtually free of cyclic structures; furthermore, they did not take into account the kinetic features of the development of the process, in particular the change in the probability of the involvement in the reaction of each of the three carboxy-groups, after the first, second, etc. group have reacted.

The opposite view concerning the importance of cyclisation reactions in three-dimensional polycondensation was reflected in a number of studies by other participants in the symposium. Referring to the considerable percentage contribution of the intramolecular cyclisation reaction even in the absence of a solvent[138], Stepto[139] examined the validity of the employment of the Kilb and Frisch theories on the basis of the available literature data (for polyesters and polyurethanes). In contrast to Flory, who excluded from consideration intramolecular cyclisation processes, both Kilb[140] and Frisch[141] described the gel formation point by the equation

$$\alpha_{\text{cr}} = \frac{1}{(f-1)(1-\lambda)},$$

where λ is a parameter absent from Flory's theory and characterising the degree of intramolecular reactions. The two authors treat λ to a certain extent differently, as a function of the concentration of the functional groups in the system at different reaction stages.

Having noted that the analogous equations proposed recently by Gordon and Scantlebury[44], Gordon and Temple[142,143], and Stamford[144] suffer from the same defect—the failure to take into account the details of the three-dimensional process (as a result of which their agreement with experiment was observed only for low degrees of conversion in the condensation reaction), Stepto proposed, on the basis of the analysis carried out, a combinatorial equation describing the critical conditions:

$$\lambda = \frac{\alpha_{\text{cr}}(f-1)-1}{(1-\alpha_{\text{cr}})\,\alpha_{\text{cr}}(f-1)} = \left(\frac{3}{2}\pi\nu b^2\right)^{\frac{3}{2}} K/N_A c_{\text{int}},$$

where c_{int} is the concentration of functional groups which have been involved in the intramolecular cyclisation reaction, ν the number of bonds in the smallest ring, b the effective bond length in the smallest ring, N_A the Avogadro number, and K a constant. The agreement between the equation and the experimental data for polyesters and polyurethanes is satisfactory in the case of polyesters according to the author.

Apart from Stepto's study dealing with the analysis of the Frisch and Kilb theories and describing the dependence of the gel formation point on the molecular structure of the components (the length and nature of the chain) as well as the reaction conditions (dilution, component ratio), a number of reports at the symposium confirmed the finding that the time has come for an experimental test of theoretical ideas and the search for and analysis of real model polymer systems.

New methods for the synthesis of model three-dimensional polymers, which permit an exact control of the number of intermolecular bonds and make it possible to guarantee a specific topology of the macromolecules, have been proposed[145,146]. According to Beinert et al.[145], model systems can be synthesised by the interaction of previously obtained linear macromolecules containing amino-groups along the entire chain with a similar polymer containing isocyanato-groups along its chain.

It has been suggested that three-dimensional macromolecules with the chain length between the network nodes specified beforehand be obtained[146] from "live" polystyrene, polyisoprene, and polyvinylpyridine macromolecules with a narrow molecular weight distribution and from branching agents—divinylbenzene or tri(allyloxy)triazine. The influence of network defects on physicomechanical properties was investigated on the models obtained and it was established that the number of "entanglements" (intertwined parts of the chain) is independent of the frequency of cross-links. According to Beinert et al.[145], the concept of the gel formation point in a three-dimensional process has lost its initial significance.

The attempts at a mathematical analysis of the dependence of the capacity of the polymer for the formation of three-dimensional structures on the chain transfer reaction in the course of the synthesis of vinyl macromolecules were described at the symposium[147]. The methods of cascade theory were used for the purpose. However, the region of applicability of the analytical expressions obtained is restricted to the reaction stages with low conversions with respect to the monomer.

The mathematical approach to the description of the dynamic behaviour of a growing three-dimensional macromolecule was used by Edwards[148]. Assuming the macroscopic behaviour of the polymer to be a consequence of the set of properties of the microscopic components, the author examined the influence of the increasing number of branching nodes in the macromolecule (intra- and intermolecular bonds, intertwined parts of the chains) on the changes in the properties of the polymer when the latter passes from the viscofluid state to the elastic state. He states that the creation of a complete dynamic theory of such systems is a more difficult problem. The problems of the study of gel formation with the aid of the new technique have been described by Wun et al.[149]

IV. CONCLUSION

In assessing the advances achieved in recent years in the development of a theory of gel formation in covalently linked three-dimensional polymers, one must note in the first place the considerable progress in the study of intramolecular interactions and cyclisation reactions of polyfunctional compounds. The solution of a number of fundamental problems of cyclisation in three-dimensional processes made it necessary to revise not only "classical" but also more modern theories of gel formation in polymers (the Gordon, Kilb, Frisch, Bruneau, etc. theories).

New experimental data showing that the functionality of the initial monomers is not a decisive factor extended the limits of the region of three-dimensional processes. In this sense, the classification of polymeric reactions involving highly functional compounds on the basis of structural features in the properties of final products can be represented as follows.

1. Reactions leading to fusible and soluble polycyclic products with a three-dimensional structure.
2. Reactions leading to polymer systems with ladder and cycloladder macromolecular structures (without gel formation).
3. Reactions proceeding in a more complex manner with simultaneous branching and cyclisation, which result in the formation of a macrogel or microgel polymer: (a) processes with insignificant degrees of cyclisation, the nature of the development of which resembles the "family tree" mechanism and which are responsible for the "homogeneous" (in the terminology of Flory[136] and other workers) formation of macrogels (the number of such reactions is evidently small); (b) processes with a fairly high degree of cyclisation proceeding via the microgel formation stage to macrogel formation; (c) processes with a high degree of intramolecular reactions leading to microgel polymers only.

The advances in the study of the early stages of the formation of three-dimensional polymers made it possible to differentiate the phenomena of micro- and macrosyneresis in a polymer–solvent system (or a polymer–low-molecular-weight reaction products system) from the phenomena involving the generation and development of three-dimensional gel particles. Taking into account these factors and also the modified concepts concerning the critical state of the system (including the "gel formation point") and the establishment of new criteria, it became possible to devise a fundamental mechanism of the process leading to covalently linked micro- and macro-gel polymers. This mechanism can include the following stages.

1. The formation of a swarm of complexes, aggregates, or globular structures via intermolecular interaction forces in solution or in the melt of polyfunctional monomers or oligomers.
2. The development of the reaction preferentially within the primary formations, or intermolecularly, or via a mixed mechanism: competing inter- and intra-molecular interactions.
3. The formation of the first microgel or macrogel particles without the manifestation of syneresis phenomena (an intermediate equilibrium state of the system containing sol and gel fractions).
4. The manifestation of micro- or macro-syneresis in the system following the breakdown of thermodynamic equilibrium.

The wide variety of the real factors associated with the physical and chemical characteristics of the initial monomers and intermediates and with the reaction conditions may lead to appreciable changes in the development of a specific process compared with the fundamental mechanism described above, for example: (a) to the coincidence of stages 3 and 4; (b) to a change in the sequence of stages—stage 4 first and stage 3 second; (c) to the absence of stage 4; (d) to the specificity of a particular stage, etc.

The development of gel formation in systems of previously obtained macromolecules can proceed via pathways different from those described and may not fit within the framework of the above mechanism. This is why the description of three-dimensional polymerisation reactions in terms of unique mathematical relations has not so far been achieved in practice. The procedures for the creation of a general theory of the formation of polymers with network and three-dimensional macromolecular structures probably require a differential investigation and description of various types of reactions of polyfunctional compounds.

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Preparation and Properties of Oligo- and Poly-phenylenes with Functional Groups

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Methods of preparing oligo- and poly-phenylenes containing various functional groups are surveyed, together with several field of application. A list of 120 references is included.

CONTENTS

I. INTRODUCTION

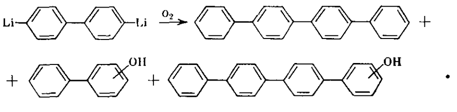
Intensive research has been undertaken during the past decade on polymers having aromatic rings in the chain and on materials based on them. Such materials are resistant not only to heat but also to various corrosive agents, including oxidants. In this respect polymers containing benzene rings in the main chain are of the greatest interest, primarily polyphenylenes, whose preparation has been reviewed several times[1-4]. However, current methods of preparation yield mainly infusible and insoluble polymers, which greatly hinders their processing and thus restricts their application.

This disadvantage might be overcome by obtaining oligophenylenes and polyphenylenes containing various functional groups. Thus polyphenylenes containing hydroxy- or carboxy-groups dissolve well in organic solvents and readily react with hydroxymethylated phenols, phenol-formaldehyde resins, oligoepoxides, metal salts, etc. to form heat-resistant, infusible cross-linked polymers[5]. The present Review surveys methods of preparation, properties, and applications of oligophenylenes and polyphenylenes containing various functional groups.

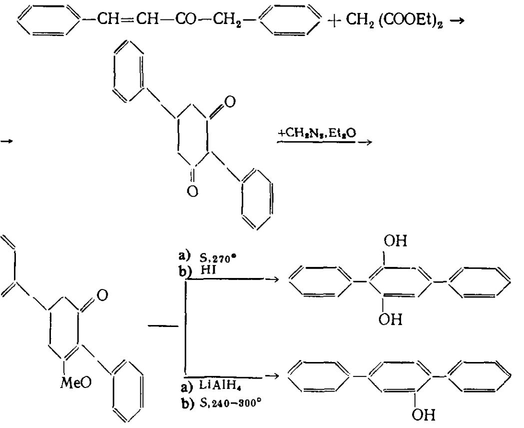
II. METHODS OF PREPARATION OF OLIGO- AND POLY-PHENYLENES WITH FUNCTIONAL GROUPS

1. Hydroxylated Oligo- and Poly-phenylenes

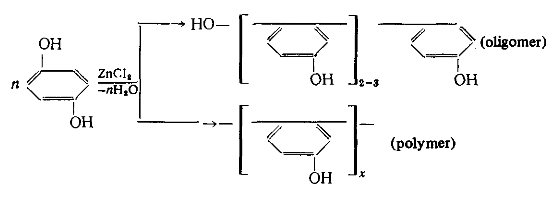
Among investigations on the preparation of hydroxylated lower oligophenylenes Pacevitz and Gilman[6] obtained *p*-phenylphenol in low yield by the oxidation with dry air of phenyl-lithium in benzene solution (at 10-15° C for 10 h). Similarly, quaterphenyl and linear oligophenylenes containing hydroxy-groups have been obtained[7] by the air oxidation of 4,4′-dilithiumbiphenyl:



The condensation of 1,4-diphenylbut-3-en-2-one with malonic ester gave[8] 2,5-diphenylcyclohexane-1,3-dione (yield ~ 80%)—the initial compound for the synthesis of *p*-terphenyl-2^5-ol (m.p. 192-193° C, yield 45%) and *p*-terphenyl-$2^{2,5}$-diol (m.p. 206-207° C, yield 35%):



Hydroxylated oligophenylenes and polyphenylenes were first obtained by Paushkin and his coworkers[9,10] by heating benzene-diols and -triols in the presence of zinc chloride (at 200-350° C for 6 h). On the basis of the infrared spectra these products were regarded as *o*-polyphenylenes (by analogy with Ref. 11):

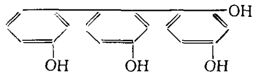
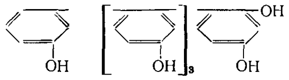
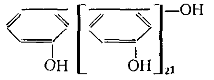


However, the suggested reaction scheme and structure of the products can only be crude approximations, since the high-temperature oxidising polycondensation of hydroxy-derivatives of benzene in the presence of a large quantity of zinc chloride may involve formation of phenyl and phenoxyl radicals, so that the structure of the products will be determined by the subsequent reactions of these radicals. Polyphenylenepolyols were obtained that were either soluble or insoluble in the usual organic solvents depending on the conditions of dehydration. Table 1 gives yields and molecular masses ($\overline{M}_n$) of soluble fractions of polyphenylenepolyols obtained from quinol, resorcinol, and pyrogallol. The yield, solubility, and molecular mass of the polymer had their maximum values in the last case. Increase in molecular mass of fractions obtained from quinol is accompanied by a sharp rise in melting point (Table 2),[9] and the polymer having $\bar{M}_n = 2020$ does not melt below 550°C.

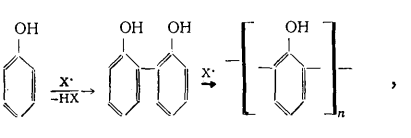
Table 1. Molecular masses and yields of hydroxylated polyphenylenes[9].

Initial diol	Yield of polymer, %		$\bar{M}_n$ of soluble fraction
	soluble fraction	insoluble fraction	
Quinol	30.6	54.4	1730
Resorcinol	67.0	9.3	1450
Pyrogallol	87.0	нет	1840

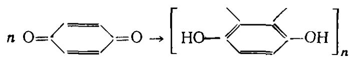
Table 2. Some characteristics of hydroxylated oligophenylene fractions from quinol[9].

Fraction	$\bar{M}_n$	Hydroxyl No., %	M.p., °C	Structure
1	330	22.8	160—180	
2	460	21.3	360—380	
3	2020	19.6	>550	

Paushkin et al. also suggested[12] polycondensation itself for the preparation of hydroxylated polyphenylenes. When phenol was heated in the presence of an equimolecular quantity of bromoform in an autoclave (at 250°C for 6 h), soluble products were obtained according to the hypothetical scheme



where $n = 4-15$ and X represents radicals formed by the thermal breakdown of bromoform. Fractionation of the polyhydroxyphenylene led to the isolation of oligomers having $n = 4-7$ (soluble in methanol) and $n \leqslant 15$ (soluble in dimethylformamide); the softening point rose from 110 to 250°C with increase in molecular mass. From the thermal stability and the composition of the hydrolysis products it was concluded[13] that the polymers had a linear structure. Polyhydroxyphenylenes soluble in alcohol, acetone, dimethylformamide, and aqueous alkalis were obtained[13] by the radical polymerisation of *p*-benzoquinone:

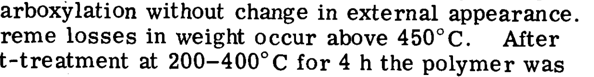


Heating phenol in the presence of iron(III) chloride at 40–90°C gave[14] poly-2-hydroxy-1,4-phenylene ("polyphenol"), an infusible dark-coloured product with $\bar{M}_n$ = 1400 (determined viscometrically), soluble only in dimethylformamide. Thermogravimetric data (ΔT = 2.5 deg min^{-1}) indicate that in an atmosphere of nitrogen the polymer begins to lose weight at 350°C, and at 900°C the losses amount to 25%. It was supposed from nuclear magnetic resonance and infrared spectroscopy together with chemical investigations that the polymer contained not only hydroxyphenylene but also cyclohexadienone groups.

2. Carboxy-containing Oligophenylenes

Berlin and his coworkers[15-21] used the Sandmeyer decomposition of bisdiazo-compounds by copper(I) salts to obtain aromatic polymers. The presence of diazo-radicals $C_6H_4.N_2^{\cdot}$ accompanying the "purely" hydrocarbon radicals leads to partial incorporation of azo-groups into the polymer chain.

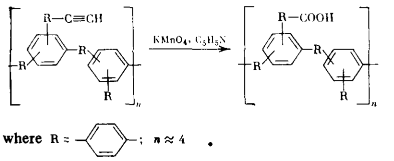
The decomposition of diazonium benzidine-3,3′-dicarboxylates[18] yielded a yellowish-brown polymer of molecular mass ~3000, which contained according to elementary analysis 1 azo-group per 6–10 benzene rings and 2 chlorine atoms per 5–16 benzene rings. Furthermore, every benzene ring contained a carboxy-group. Infrared spectroscopy suggested linear or slightly branched polymers[20], with either chlorine or peroxy as terminal groups. The structure of the products was therefore represented by the formula[18]



However, the general formula given is extremely arbitrary, and may not correspond to the true structure of the polymer molecule, since not only the structure of the blocks but also the alternation of azo-groups in the chain may be represented in other ways.

When heated in argon at 400°C for 1 h or at 250–400°C for 4 h, carboxylated oligophenylenes undergo complete decarboxylation without change in external appearance. Extreme losses in weight occur above 450°C. After heat-treatment at 200–400°C for 4 h the polymer was insoluble both in dimethylformamide and in aqueous alkalis[17].

Oligophenylenecarboxylic acids have been obtained[22,23] by oxidising oligophenylenes containing various carbon–carbon multiple bonds. Fractions having $\bar{M}_n$ = 1000–2200, obtained by the polycyclotrimerisation of a mixture of *p*-diethynylbenzene at phenylacetylene in the presence of various catalysts[24-26]—$TiCl_4.Al(iso\text{-}C_4H_9)_3$, $NiCl_2.2P(C_6H_5)_3 \times 2NaBH_4$, $Ni(C_5H_7O_2)_2.P(C_6H_5)_3$, and $[(C_2H_5O)_3P]_4CoBr$—and soluble in benzene and pyridine but insoluble in alcohol, were chosen for oxidation. Potassium permanganate was used[23] to oxidise the oligophenylenes (e.g. containing terminal ethynyl groups) by heating in pyridine solution:



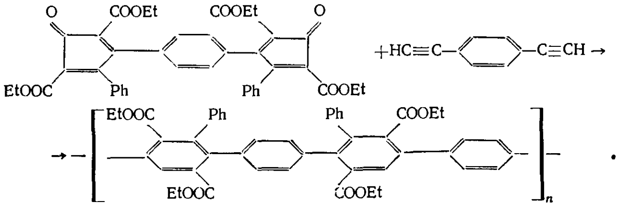
The resulting oligophenylenecarboxylic acids were light grey powders, soluble in pyridine, dioxan, oxolan, etc. Depending on the structure of the initial oligomer they had melting points of 130–280°C and acid numbers of 63–80. When the oligomeric acids were heated in argon they underwent decarboxylation, whose rate became appreciable only at 220–230°C. The resulting oligophenylenes were readily soluble in benzene, their molecular masses were closely similar to those of the original oligomers before oxidation, and they contained no carboxyls. Differential thermal analysis in helium ($\Delta T = 4.5$ deg min^{-1}) indicated that the oligomeric acids began to lose weight at ~ 230°C, vigorous decomposition occurred from 350–370 to 650°C, and the yield of the carbon residue at 900°C was 55% of the original weight of the specimen.

Oligophenylenecarboxylic acids obtained by oxidising oligophenylenes containing multiple bonds can be used as starting materials for the preparation of polyethers, polyesters, and polyamides.

3. Alkoxycarbonylated Oligo- and Poly-phenylenes

Methyl oligophenylenecarboxylates of molecular mass 1800, containing ~ 4 methoxycarbonyl groups in the oligomeric molecule, were obtained by treating the oligomeric acids with a solution of diazomethane in toluene[28]. They were grey powders, readily soluble in benzene, dioxan, chloroform, etc.

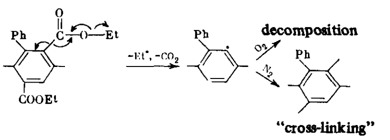
Harris and Reinhardt[27] synthesised ethoxycarbonylated oligo- and poly-phenylenes by the Diels–Alder reaction from ethoxycarbonylated biscyclopentadienones and aromatic diynes. Thus treatment of diethyl 2-oxo-4,5-diphenylcyclopentadiene-1,3-dicarboxylate with *p*-diethynylbenzene in benzene gave an approximately 97% yield of tetraethyl $1^1,1^6,3^3,3^4$-tetraphenyl-*p*-terphenyl-$1^2,1^5,3^2,3^5$-tetracarboxylate (a white powder melting at 223–224°C and readily soluble in chlorinated hydrocarbons). Similarly, ethyl carboxylates of polyphenylenes have been obtained by reaction between tetraethyl *p*-phenylenebis-4-(2-oxo-5-phenylcyclopentadiene-1,3-dicarboxylate) and *p*-diethynylbenzene in 1,1,2,2-tetrachloroethane solution:



The equation arbitrarily shows formation of a substituted poly-*p*-phenylene, although the conditions of the Diels–Alder reaction indicate the formation of both *meta*-linked and *para*-linked aromatic rings. The products had $\eta_{\log} \simeq 3.0$ (determined at a polyphenylene concentration of 0.25 g dl^{-1} in 1,1,2,2-tetrachloroethane solution at 30°C), and formed colourless, transparent films, whose infrared spectra coincided with those of model compounds.

Differential thermal analysis showed that ethoxycarbonylated polyphenylenes begin to lose weight in the air only at 370°C, and are completely decomposed when heated to 520°C. In nitrogen intense loss of weight occurs above 370°C, and at 800°C the yield of carbon residue is 55%. Infrared spectroscopy indicated[27] that the losses in weight at 370–450°C are due to decarboxylation. Under isothermal conditions films undergo decarboxylation in nitrogen even below 300°C, with the formation of insoluble products.

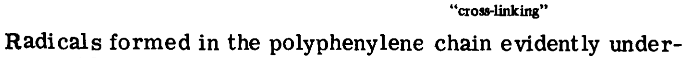
The above facts were explained[27] on the hypothesis of a free-radical mechanism for decarboxylation:



Radicals formed in the polyphenylene chain evidently undergo rapid oxidation in air. In an atmosphere of nitrogen free radicals either abstract hydrogen, giving rise to "cross-linking", or become involved in reactions leading to graphitic structures.

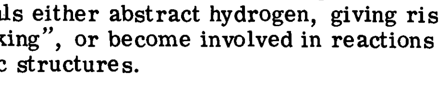
4. Methoxylated Oligophenylenes

Methoxylated oligophenylenes are readily formed under the conditions of the Ullmann reaction. Thus 3,3′,5,5′-tetramethoxybiphenyl (m.p. 208°C) was obtained by heating 4-iodo-2,6-dimethoxybenzene in the presence of copper powder at 220–260°C.[28] When 4-iodo-4′-methoxybiphenyl was heated in the presence of copper bronze at 280°C for 1 h, $1^4,4^4$-dimethoxy-*p*-quaterphenyl (m.p. 338–340°C) was formed[29]:

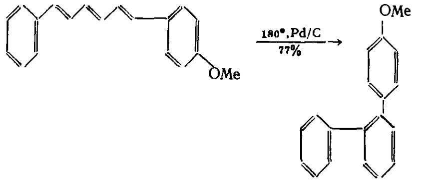


(A)

Under conditions of oxidising dimerisation the yield of (A) is far lower[29]:



Pyrolysis of 1-*p*-methoxyphenyl-6-phenylhexa-1,3,5-triene in the presence of a palladium–carbon catalyst (10% by weight) *in vacuo* at 180°C gave *p*-methoxy-*o*-terphenyl (a colourless oil boiling at 153°C under 0.2 mmHg)[30]:



Several methoxylated *p*-oligophenylenes—from biphenyl to octophenyl—were synthesised by Kern et al.[28] from cyclic ketones and lithium aryls via intermediate hydroaromatic compounds:

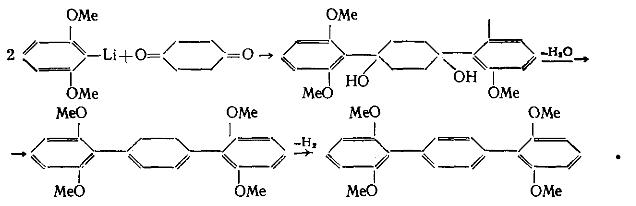
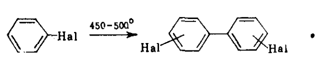


Table 3 gives the properties of the products with for comparison those of their unsubstituted analogues. It is evident that in all cases a methoxy-derivative melts at a lower temperature and dissolves better in toluene than the corresponding unsubstituted *p*-oligophenylene.

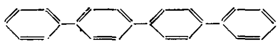
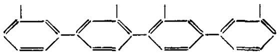
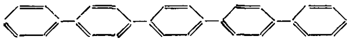
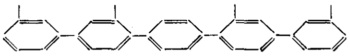
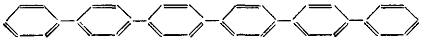
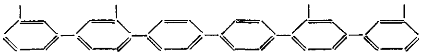
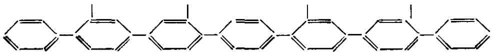
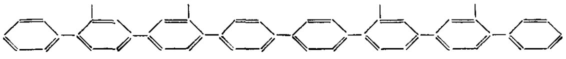
5. Halogenated Oligo- and Poly-phenylenes

Halogenated biphenyls are formed by the high-temperature treatment of halogenobenzenes: e.g. [31]

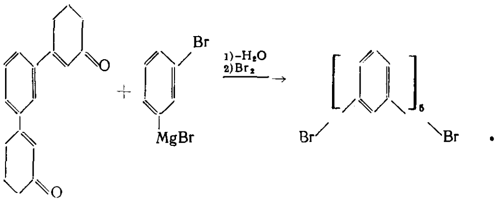


Chlorobiphenyls were found[32] among products of the pyrolysis of a mixture of *p*-nitrotoluene and chlorobenzene (at 600°C for 20 s).

Table 3. Melting points and solubilities in toluene (at 20°C) of methoxylated *p*-oligophenylenes [28].

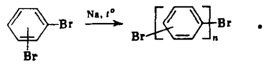
Formula	M.p., °C	Solubility, g litre^{-1}
	320	0.22
	158	22.0
	395	0.1
	165	3.5
	475	0.01
	210	2.0
	545	—
	253	0.5
	277	0.2

An interesting method[33] was used to obtain *m*-oligophenylenes containing bromine at the ends of the polymer chain:

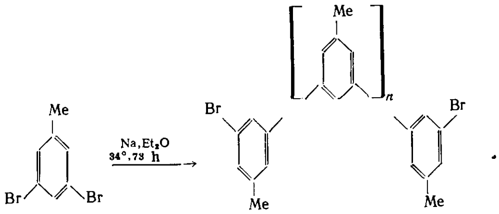


Reaction of *m*-dicyclohexenylbenzene-3′,3″-dione with *m*-bromophenylmagnesium bromide followed by dehydration and aromatisation gave a 9% yield of $1^3,5^3$-dibromo-*m*-quinquephenyl, a yellow–orange powder of m.p. 104–106°C (from alcohol). $1^3,3^3$-Dibromo-*m*-terphenyl (an uncrystallisable oil) and $1^3,6^3$-dibromo-*m*-sexiphenyl (melting at 143–145°C) were synthesised by similar methods. A multistage process is involved, and the yield of the desired product does not exceed 10%.[33]

The Wurtz–Fittig reaction has been successfully applied to the synthesis of halogenated oligophenylenes. As early as 1886 Goldschmiedt[34] obtained amorphous yellow powders, melting over the ranges 200–250 and 245–300°C, by heating *m*- and *p*-dibromobenzenes respectively with metallic sodium in ether. The reaction can be represented by the scheme (n = 8–13)



A mixture of oligomeric products having n = 2–4 and 6, containing *meta*-substituted groups, was obtained by the polycondensation of 3,5-dibromotoluene under the influence of metallic sodium[35]:



The polycondensation of *p*-dichlorobenzene in the presence of metallic sodium or a sodium–potassium alloy gives a reddish-brown powder soluble in aromatic hydrocarbons and not melting below 550°C.[36,37] Elementary analysis indicates that the polymer molecule contains ~ 5 chlorine atoms. The structure is assumed to contain not only *p*-phenylene but also *p*-quinoid groups.

A patent[38] describes the synthesis of *αω*-dibromo-*p*-polyphenylenes from *p*-dibromobenzene in a dioxan–xylene medium under the influence of metallic sodium.

Kovačic and his coworkers[39–42] undertook the oxidative dehydropolycondensation of benzene in various organic solvents—carbon disulphide, benzene, dichlorobenzene, etc.—in the presence of the $AlCl_3$–$CuCl_2$ catalytic system, and obtained polyphenylenes containing chlorine. When the reaction was accomplished in the presence of iron(III) chloride[43,44], small quantities of lower products, e.g. chlorobenzene, 4,4′-dichlorobiphenyl, etc., were also formed. This work showed that the thermo-oxidative stability of *p*-polyphenylenes increases with the chlorine content of the polymer (Table 4). When benzene underwent oxidative dehydropolycondensation in the presence of antimony(V) chloride, the polyphenylenes contained up to 31% of chlorine[40,45].

Table 4. Losses in weight of chlorinated poly-*p*-phenylenes in air (ΔT = 8 deg min^{-1}).[43,44]

Temp., °C	Loss (%) for Cl content		Temp., °C	Loss (%) for Cl content	
	6.0%	23.6%		6.0%	23.6%
350	0.49	0.35	500	55.50	15.55
400	0.99	0.94	550	97.00	73.0
450	16.15	2.70	600	100	99.9

Some Japanese investigators[46–48] obtained polyphenylenes by decomposing biphenyl-4,4′-bisdiazonium dichloride in aqueous solution in the presence of copper(I) and iron(II) chlorides at 50–80°C. In the polymer having $\bar{M}_n$ = 10 000 one chlorine atom was present per 3–4 benzene rings. The polymer dissolved in benzene, oxolan, dioxan, and chloroform[49]. Examination of fractions of molecular mass 3000–5000 showed the presence of 5–8 azo-groups per molecule[47]. A radical mechanism was assumed for the formation of polyphenylenes[50].

Detailed information on the preparation and properties of fluorinated oligophenylenes and polyphenylenes has recently been surveyed[51].

6. Alkylated Oligo- and Poly-phenylenes

Among the first syntheses of methylated oligophenylenes was that of $1^4,4^4$-dimethyl-*p*-quaterphenyl (m.p. 340°C) by heating 4-iodo-4′-methylbiphenyl in the presence of copper bronze[52]:

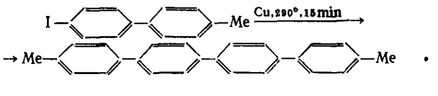
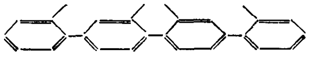
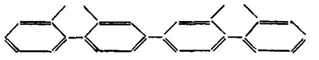
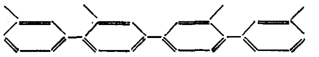
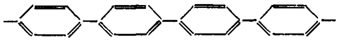
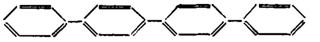
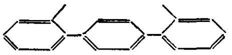
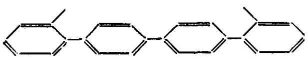
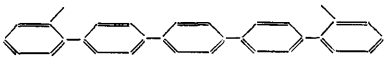
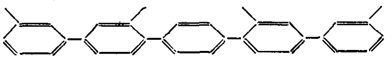
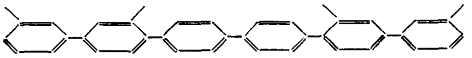
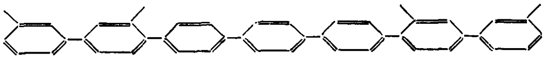
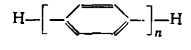
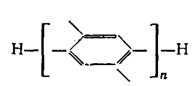
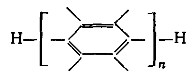


Table 5. Melting points and solubilities in toluene of methylated *p*-oligophenylenes[53–55].

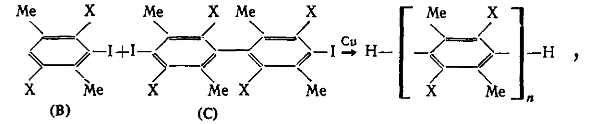
No.	Formula	M.p., °C	Solubility, g litre⁻¹
1		84	500
2		96	470
3		139	110
4		340	0.2
5		320	0.13
6		146	42
7		150	51
8		231	1.3
9		186	11
10		200	9.5
11		261	1.1

Wirth et al.[53] used the Ullmann reaction in the presence of copper powder at 230–260°C to prepare a series of methylated *p*-oligophenylenes (yield 40–50%)[53–55]. Some properties of the resulting oligomers are given in Table 5. These workers showed that the introduction of methyl groups into the $1^4,4^4$-positions of *p*-quaterphenyl (No. 5 in Table 5) has hardly any effect on the melting point or the solubility in toluene; the introduction of methyl groups into the *ortho*- and *meta*-positions lowers the melting point of the products and improves significantly their solubility in toluene. Increase in the number of methyl groups in the *p*-quinquephenyl molecule lowers the melting point and enhances the solubility in toluene (No. 8 and 9). Yet increasing the number of unsubstituted benzene rings in methylated oligophenylenes raises the melting point and lowers the solubility (No. 6–8 and 9–11). Thus methylated *p*-oligophenylenes have lower melting points and better solubility than have their unsubstituted analogues, and the solubility is better the greater the number of methylated benzene rings.

Table 6. Melting points and solubilities in toluene of *p*-oligophenylenes containing di- and tetra-methylbenzene rings[56].

No.	Formula	Degree of condensation n	M.p., °C	Solubility, g litre⁻¹
1		2	71	430.0
		3	215	7.4
		4	320	0.13
		5	395	0.005
2		2	54	700.0
		3	183	28.0
		4	266	1.1
		5	309	0.24
3		2	137	365.0
		3	272	24.0
		4	272	3.4

Oligophenylenes comprising *p*-xylene and *p*-durene units were obtained by the Ullmann reaction[56]:

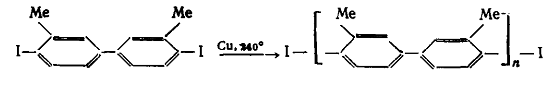


where n = 2–5 and X = H, CH_3. The highest yield (50%) of such oligophenylenes is obtained with reactants B and C in the molar proportions 10 : 1. Table 6 shows that the melting points of both unsubstituted (No. 1) and di- and tetra-methylated *p*-oligophenylenes (No. 2 and 3) rise and the solubilities in toluene diminish with increase in the degree of condensation.

Table 7. Molecular masses and melting points of fractions of methylated polyphenylene obtained by the Ullmann reaction[57].

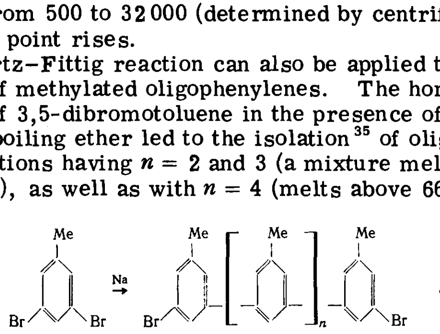
Fraction	M.p., °C	$\bar{M}_w$
1	290–310	32 000
2	225–245	3 700
3	120–140	500

The Ullmann reaction was used also for the synthesis of *p*-oligophenylenes containing a methyl group in every benzene ring[57]. The soluble methylated polyphenylenes obtained by the reaction



were fractionated by centrifugation and osmometry, when a fraction of molecular mass 300 000 was isolated. The cryoscopic method gave anomalous values of the number-average molecular mass. It was concluded[57] from viscosity, sedimentation, and diffusion results that under the given reaction conditions the polymeric molecules probably had not a linear but a branched structure, with *m*-phenylene groups in the main chain. Table 7 shows that with increase in the weight-average molecular mass of the fractions from 500 to 32 000 (determined by centrifugation) the melting point rises.

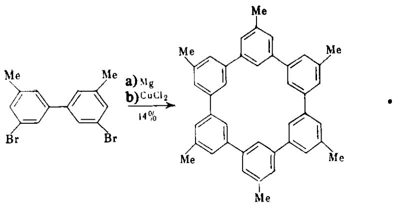
The Wurtz–Fittig reaction can also be applied to the synthesis of methylated oligophenylenes. The homocondensation of 3,5-dibromotoluene in the presence of metallic sodium in boiling ether led to the isolation[35] of oligophenylene fractions having $n = 2$ and 3 (a mixture melting below 60°C), as well as with $n = 4$ (melts above 66°C) and $n = 6$:



Each of these fractions is an amorphous yellow powder soluble in benzene and ether.

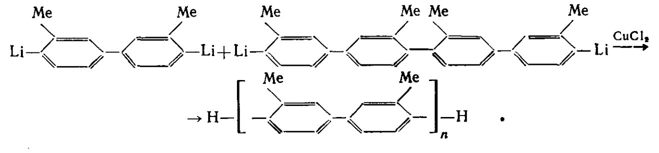
The synthesis of a methylated *p*-oligophenylene by the reaction of 4,4′-di-iodo-3,3′-dimethylbiphenyl with metallic sodium in boiling toluene was reported[58]. The resulting polymer was soluble in benzene, and melted at 150–180°C.

Organomagnesium compounds can also be used for the preparation of methylated oligophenylenes from halogenated aromatic compounds. Thus Kern et al.[59] obtained an oligophenylene by treating 4,4′-di-iodo-3,3′-dimethylbiphenyl with magnesium at 20°C. They noted that linear oligophenylenes were not formed, and concluded that the Grignard reaction, despite the milder conditions, is less suitable than the Ullmann reaction for obtaining oligophenylenes of regular structure. Bräunling et al.[60] used the Grignard reaction to synthesise methylated cyclic *m*-oligophenylenes. Thus hexamethylhexa-*m*-phenylene (m.p. 452–453°C) was obtained from 3,3′-dibromo-5,5′-dimethylbiphenyl:



3,3′-Dibromo-6,6′-dimethylbiphenyl gave a low yield of octamethylocta-*m*-phenylene (m.p. 489°C).

Furthermore, the oxidative dimerisation of dilithium derivatives of methylated aromatic compounds yields methylated oligophenylenes[61]. When a mixture of 4,4′-dilithium-3,3′-dimethylbiphenyl and $1^4,4^4$-dilithium-$1^2,2^2,3^2,4^3$-tetramethyl-*p*-quaterphenyl is treated with copper(II) chloride, methylated *p*-oligophenylenes having $n = 4$ and 6 are formed:



Similarly, $1^2,2^3,3^2,4^3,5^2,6^3,7^2,8^3$-octamethyl-*p*-octophenyl (m.p. 273°C) was obtained, together with small quantities of products having $n > 8$, from 1^4-lithium-$1^2,2^3,3^2,4^3$-tetramethyl-*p*-quaterphenyl.

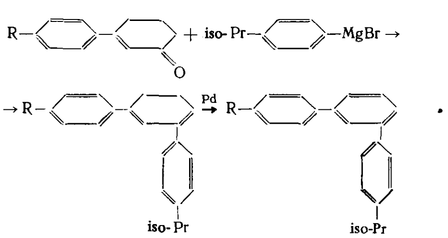
Reduction of 4-acetyl-4′-ethylbiphenyl on zinc amalgam in an acid medium gave 4,4′-diethylbiphenyl[62], which after recrystallisation from ethanol melted at 81°C.

Methylated oligophenylenes can be obtained from aromatic compounds not only by the above condensation methods but also by processes involving the formation of new benzene rings by the aromatisation of C_6 cyclic systems, as well as cycloaddition and cyclisation.

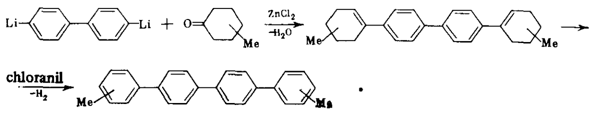
Table 8. Melting points and solubilities of methylated *p*-quaterphenyls[64].

No.	Positions of methyl	M.p., °C	Solubility, g litre^{-1}	No.	Positions of methyl	M.p., °C	Solubility, g litre^{-1}
1	1^2-	172—173	26.0	5	1^3, 4^3-	214—215	6.3
2	1^3-	244—245	3.0	6	1^4, 4^4-	338—340	0.2
3	1^4-	328—330	1.2	7	unsubst.	320	0.1
4	1^2, 4^2-	150—151	36.0				

Reaction of phenylcyclohexenone with *p*-isopropylphenylmagnesium bromide gave a diarylcyclohexadiene, whose dehydrogenation over palladium yielded an isopropyl-*m*-terphenyl[63]:



Organolithium compounds have been especially widely used in the synthesis of methylated oligophenylenes from cyclic ketones. Thus the condensation of 2-, 3-, and 4-methylcyclohexanones with 4-lithium-*p*-terphenyl or with 4,4′-dilithiumbiphenyl gave products from which the corresponding 1-methyl- and 1,4-dimethyl-*p*-quaterphenyls (Table 8) were obtained by dehydration in the presence of zinc chloride and dehydrogenation by means of chloranil in boiling xylene[64]:



Introduction of a 4-methyl group into *p*-quaterphenyl somewhat raises the melting point (cf. No. 6 and 3 with No. 7 in Table 8). Introduction of a methyl group at position 3 and especially at position 2 (cf. No. 2 and 5; 1 and 4 with No. 7) improves the solubility in toluene and lowers the melting point of the products. These effects are still more strongly developed in dimethyl-*p*-quaterphenyls substituted at the 2 or 3 positions (No. 4 and 5).

Methylated derivatives of *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, *p*-sexiphenyl[55], and *p*-octophenyl[7] were obtained from cyclic diketones (cyclohexa-1,4-dione and bicyclohexyl-4,4′-dione) and lithium aryls via intermediate hydroaromatic compounds.

Somewhat later it was shown[53,54] that the increased solubility of methylated *p*-oligophenylenes obtained by the Ullmann reaction is explained by breakdown of symmetry of the compounds due to the combined effects of substitution and rotation, the latter associated with diminished symmetry resulting from internal molecular mobility (rotation of rings).

p-Oligophenylenes with $n \leqslant 14$ and containing one or two unsubstituted *m*-phenylene units in the main chain were synthesised[65]:

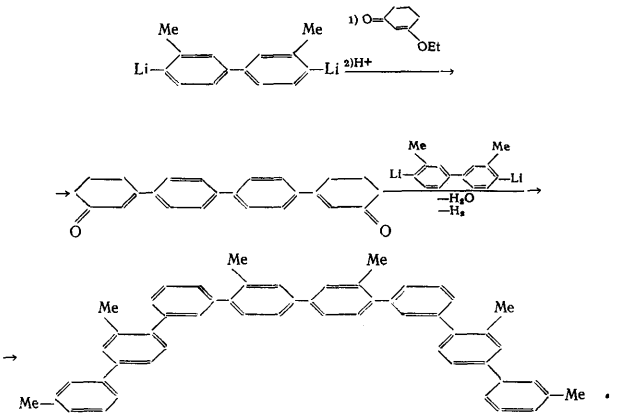


Table 9. Melting points and solubilities in toluene (at 20°C) of methylated oligophenylenes[65].

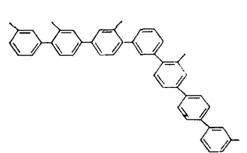
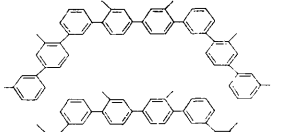
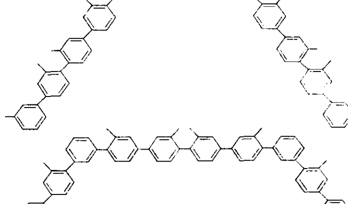
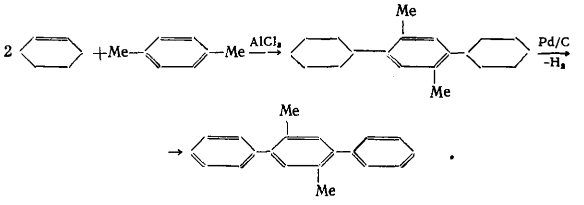
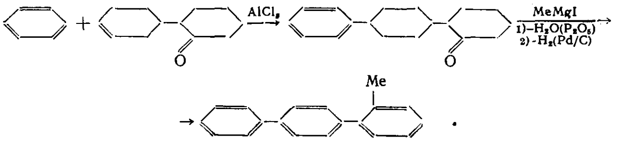
No.	Formula	M.p., °C	Solubility, g litre-1
1.		202—203	12
2.		170—171	73
3.		221—222	12
4		218—220	10

Table 9 gives the melting points and solubilities in toluene of several methylated oligomers of this type. Their infrared spectra are identical with those of *p*-oligophenylenes, whereas the ultraviolet spectra differ appreciably; the melting points are lower and the solubilities better than for the corresponding *p*-oligophenylenes.

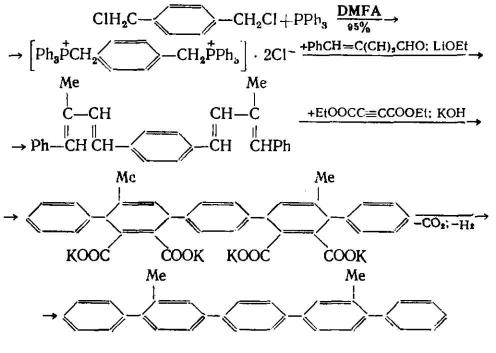
Methylated *p*-terphenyls have been obtained also by the Friedel–Crafts reaction. Deuschel[66] condensed cyclohexene with *p*-xylene in carbon disulphide in the presence of aluminium trichloride to give 2,5-dicyclohexyl-*p*-xylene, which was then dehydrogenated over a palladium–carbon catalyst to $2^2,2^5$-dimethyl-*p*-terphenyl:



1^2-Methyl-*p*-terphenyl (m.p. 91–92°C) was obtained[67] from products of the condensation of 2-cyclohex-3′-enylcyclohexanone with benzene in the presence of aluminium chloride:

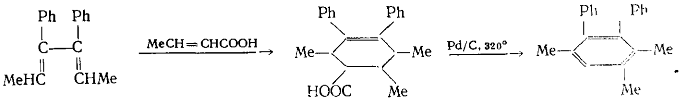


Campbell and McDonald[68] synthesised dimethyl-*p*-quinquephenyls, using cyclisation to introduce the methylated rings. Thus the reaction of *p*-xylenebistriphenylphosphonium dichloride with α-methylcinnamaldehyde gave *p*-bis-3-methyl-4-phenylbutadienylbenzene, which on the cycloaddition of diethyl acetylenedicarboxylate in the presence of potassium hydroxide formed potassium tetrahydro-$2^2,4^3$-dimethylquinquephenyltetracarboxylate, whose dehydrogenation and decarboxylation yielded $2^2,4^3$-dimethyl-*p*-quinquephenyl (m.p. 217–218°C):

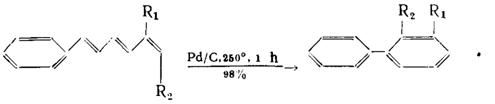


When *p*-methylcinnamaldehyde was used as initial compound, $1^4,5^4$-dimethyl-*p*-quinquephenyl (m.p. 400°C) was obtained.

Langer and Wessely[69] synthesised several methylated *o*-, *m*-, and *p*-terphenyls by the dehydrogenation over a palladium–carbon catalyst of substituted cyclohexenes—products of the cycloaddition of e.g. an acrylic acid to a buta-1,3-diene:

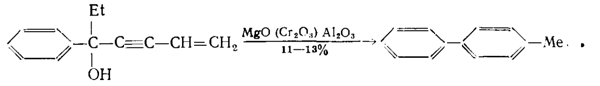


Methylated biphenyls may be formed by the high-temperature cyclisation of the side-chains of various aromatic compounds. Thus mono- and di-methylbiphenyls were obtained[30] by heating phenylalkatrienes in the presence of a palladium–carbon catalyst in a vacuum to 250°C:

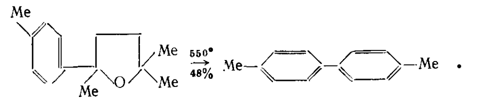


R_1=H or Me; R_2=Me

Substituted biphenyls were obtained from benzene derivatives containing at least six carbon atoms in the side-chain[70–73] (e.g. unsaturated compounds—1-ethyl-1-phenylpent-4-en-2-ynol, 1,4,4-trimethyl-1-phenylbutynediol, etc.) in the presence of a chromium–alumina catalyst:



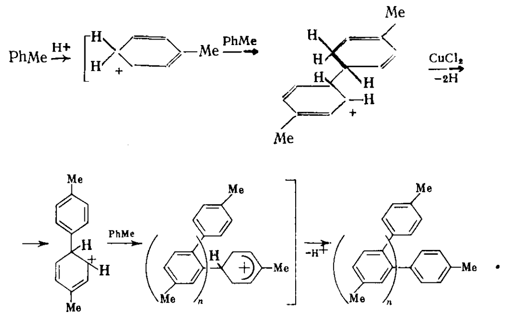
The pyrolysis of 2,2,5-trimethyl-5-*p*-tolyloxolan at 550°C yields 4,4′-dimethylbiphenyl (m.p. 121°C)[74]:



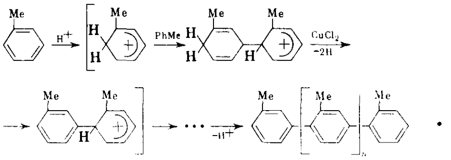
Oxidative dehydropolycondensation is currently among the best known and simplest methods for synthesising polymers having aromatic groups in the main chain. First developed by Kovačic and his coworkers in 1962,[75] it enables polyphenylenes to be obtained by the single-stage conversion of aromatic compounds in the presence of catalysts such as Lewis acids and oxidising agents at 30–37°C[39,41,42,75,76]. Several investigations have shown[43,77,78] that the oxidative dehydropolycondensation of benzene usually gives polymers that are infusible and insoluble in organic solvents. Mixtures of benzene with various aromatic hydrocarbons—e.g. naphthalene, biphenyl, terphenyl, toluene, xylenes, etc.—were proposed[79–87] for the production of fusible and soluble polyphenylenes. The properties of the resulting polymers were found to depend mainly on the process conditions (proportions and concentrations of initial monomers, catalyst concentrations, type of solvent, temperature, etc.).

Oxidative dehydropolycondensation is catalysed most effectively[41–43,77] by the aluminium(III)–copper(II) chloride system. In its presence toluene yielded oligophenylenes of mean degree of polymerisation n = 10–20, soluble in aromatic hydrocarbons (benzene, toluene) and having m.p. ≃ 250°C. Nuclear magnetic resonance, infrared, and ultraviolet spectroscopy together with elementary analysis of the oligophenylenes and of products formed under conditions of oxidative degradation showed that the main oligomer chain consisted of *ortho*-linked aromatic rings containing *p*-methyl groups. A certain number of *para*-linked phenylene units were also present in the chain. From this Kovačic and Ramsey[87] suggested that the mechanism of the formation of *o*-oligophenylenes from toluene (the ring bonds are delocalised) was

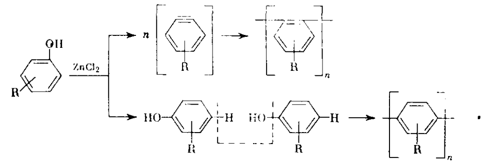
$$H_2O + AlCl_3 \rightleftarrows H_2O \ldots AlCl_3 \rightleftarrows H^+[AlCl_3(OH)]^-;$$



When a benzonium ion protonated *ortho* to the methyl group appears, growth of the oligomeric molecule leads to formation of a methylated *p*-oligophenylene:



Alkylated polyphenylenes were obtained by Paushkin et al.[9,88] by oxidative polycondensation of the corresponding phenols. Thus phenol and its homologues (*m*-cresol, *p*-t-butylphenol, etc.) in the presence of zinc chloride (at 250–350°C for 6 h) gave polymers partly soluble in dimethylformamide, phenol, pyridine, dioxan, and concentrated sulphuric acid. The solubility of the polymers diminished with rise in temperature and increase in duration of the reaction. The mechanism was regarded as involving dehydration and polymerisation of an intermediate dehydrobenzene or as polycondensation:

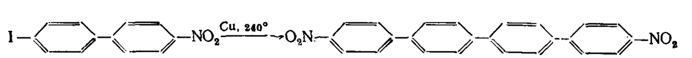


The former was regarded as the more probable, since polymers with *ortho*-linked benzene rings were mainly formed. However, the suggested mechanism can hardly be regarded as soundly based, since intermediate formation of dehydrobenzene is unlikely in the high-temperature conversion of phenols in the presence of catalysts. Processes involving phenoxy-radicals and their subsequent conversion products probably also take place under these conditions.

The unsubstituted or alkylated *o*-phenylenes (yield ⩽ 32%) obtained from phenol, *m*-cresol, and *p*-t-butylphenol respectively contained 9.8–19.6% of soluble fractions having $\overline{M}_n$ = 950–1050. The presence of a small quantity of oxygen in the polymer is evidently due to terminal hydroxyls[88].

7. Nitro-substituted Oligo- and Poly-phenylenes

Several nitro-*p*-quaterphenyls were synthesised in order to ascertain the influence of nitration on the solubility of oligophenylenes. Thus $1^4,4^4$-dinitro-*p*-quaterphenyl, obtained from 4-iodo-4′-nitrobiphenyl by the Ullmann reaction[29]



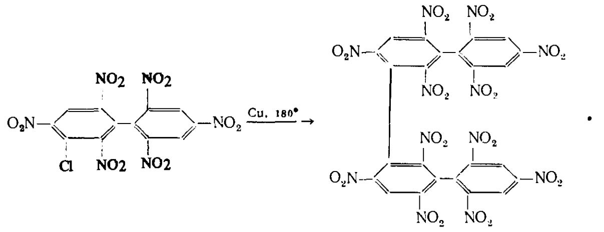
was isolated as yellow crystals of m.p. 317–320°C, insoluble in the majority of organic solvents.

Table 10. Solubilities in toluene (at 20°C) and melting points of nitrated and methylated *p*-quaterphenyls[89].

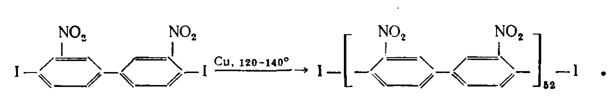
Substituted at positions	Nitro-derivative		Methyl derivative	
	solubility, g litre^{-1}	m.p., °C	solubility, g litre^{-1}	m.p., °C
2^3-	4.3	288	—	—
2^3, 3^2-	3.4	342	55	178
1^3, 4^3-	3.8	233	51	150
1^2, 2^2, 3^3, 4^2-	2.0	207	3.5	213
$1^{2,4}$, 2^3, 3^2, $4^{2,4}$-	0.85	235	470	96
	0.20	292	—	—

Comparison of the properties of methylated and nitrated *p*-quaterphenyls showed (Table 10) that the latter have rather higher melting points, but considerably lower solubilities, than their methylated analogues[89]. On the whole a nitro-group produces little enhancement of the solubility of oligophenylenes, although in polar solvents (nitrobenzene, dimethylformamide) their solubility is increased significantly.

From 3-chloro-2,2′4,4′,6,6′-hexanitrobiphenyl in dry nitrobenzene in the presence of copper bronze Dacons[90] obtained dodecanitroquaterphenyl (yield 70%), an explosive compound:

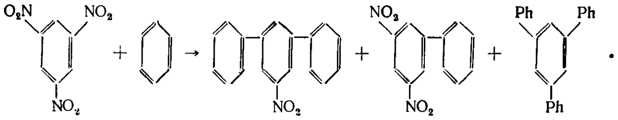


A nitro-substituted *p*-polyphenylene was obtained by the Ullmann reaction, when 4,4′-di-iodo-3,3′-dinitrobiphenyl in dimethylformamide solution in the presence of copper bronze was heated to 140°C[89]:



The polymer was a crystalline yellow powder, infusible and insoluble, which decomposed above 250°C.

As an alternative to the main method for obtaining nitrated oligophenylenes—the Ullmann reaction—the pyrolysis of aromatic compounds can be used for nitroterphenyls and nitrobiphenyls. Fields and Meyerson[32,91] studied the arylation of aromatic nitro-compounds at high temperatures. A 28% yield of 3-nitrobiphenyl was isolated from the pyrolysis of a mixture of *m*-dinitrobenzene and benzene (molar proportions 1 : 10) at 450°C. The reaction between 1,3,5-trinitrobenzene and benzene at 450–600°C gave a mixture of nitroterphenyl, dinitrobiphenyl, and triphenylbenzene:

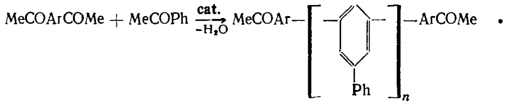


A radical mechanism is involved with intermediate formation of a phenyl radical:

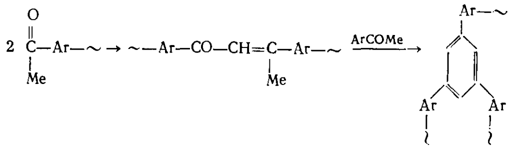
$$PhNO_2 \rightarrow Ph^{\cdot} + NO_2 \ .$$

8. Oligophenylenes containing Acetyl and Acetal Groups

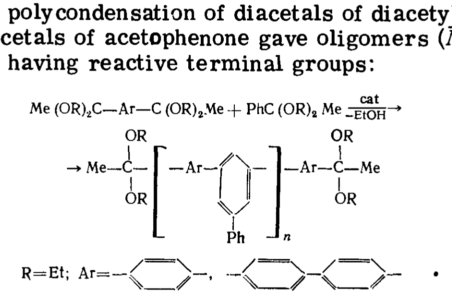
Oligophenylenes having terminal acetyl groups were first synthesised by Korshak et al.[92–94] by the polycyclocondensation of mono- and di-acetylated aromatic compounds. In the presence of an acid catalyst (hydrogen chloride, sulphuric acid, toluene-*p*-sulphonic acid) at 20°C infusible oligophenylenes, having $\bar{M}_n$ = 1500–4200, containing acetyl end-groups, and soluble in benzene, toluene, chloroform, and other organic solvents, were obtained from acetophenone with *p*-diacetylbenzene or with 4,4′-diacetylbiphenyl:



Trimerisation was shown to involve intermediate formation of a dimer containing dypnone fragments, which interacted with the acetyl group to give the 1,3,5-trisubstituted benzene rings:



The introduction of ethyl orthoformate promoted conversion of the acetyl compounds into acetals, which readily trimerised to a benzene ring. Korshak et al.[95–97] suggested that acetylated aromatic compounds should be replaced by their acetals as initial compounds, in order to diminish the significance of side-reactions in the synthesis and lower the quantity of defective structures in the polymer. The polycondensation of diacetals of diacetylarylenes with acetals of acetophenone gave oligomers ($\bar{M}_n$ = 1700–2500) having reactive terminal groups:

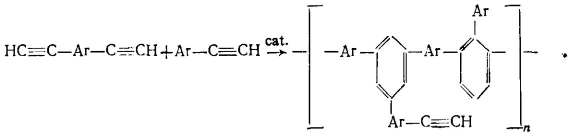


A linear structure was attributed to the resulting oligophenylenes on the basis of their elementary composition, molecular mass, and proton magnetic resonance spectra.

The oligophenylenes obtained either from acetylated aromatic compounds or from their acetals, when heated (at 400°C in the absence of a catalyst or at 300°C in the presence of toluene-*p*-sulphonic acid), set to infusible and insoluble products. Thermogravimetric results indicated that these products began to decompose at 430°C when heated in helium, and at 900°C the total losses in weight were 30%.

9. Ethynylated Oligophenylenes

The controlled synthesis of soluble aromatic polymers by the polycyclotrimerisation of a mixture of butadiyne and acetylene in an inert organic solvent, with the use of tantalum and niobium halides and oxide halides as catalysts between −30 and +200°C, was reported in the patent literature[98-100]. The chains in such polymers may terminate in ethynyl groups. Little study has been made of the properties of the products. Strongly branched oligophenylenes with terminal ethynyl groups have been obtained by the copolycyclotrimerisation of mono- and diacetylenic compounds in the presence of various catalytic systems (such as $[(AlkO)_3P]_4CoBr$,[101-103,24] $2NaBH_4.2(C_6H_5)_3P.NiCl_2$,[104] Ziegler catalysts[105], and other transition-metal complexes):



Oligophenylenes containing ethynyl groups and having molecular weights $\overline{M}_n$ = 1000–2500 (determined ebullioscopically in benzene) dissolve readily in benzene, toluene, and other organic solvents. The polymers easily set at 150–250°C to hardened products possessing high deformation heat-resistance, which increases with the number of ethynyl groups in the initial copolymer. However, the stability towards thermal oxidation of the hardened polyphenylenes diminishes with increase in the number of ethynyl groups.

Analogous soluble branched oligophenylenes having terminal ethynyl groups were obtained by Bracke[106] by the copolycyclotrimerisation of *m*-diethynylbenzene and phenylacetylene in chlorobenzene in the presence of a Fisher type of catalyst $TiCl_2.2AlCl_3$ at temperatures from −35 to +20°C. Thermogravimetry indicated that the polymer began to decompose at ~ 500°C whether in an inert gas or in air.

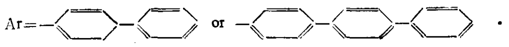
Furthermore, oligophenylenes having $\overline{M}_n$ = 10 000 (determined by gel-permeation chromatography), soluble in benzene and chlorinated hydrocarbons, were obtained by Chalk and Gilbert[107] by the copolycyclotrimerisation of phenylacetylene and *m*-ethynyltoluene with *m*-diethynylbenzene in the presence of a Ziegler catalyst (in toluene between −23 and +20°C). The products softened at 200–300°C depending on the molecular mass. The polymers were processed by extrusion.

10. Alkenylated Oligophenylenes

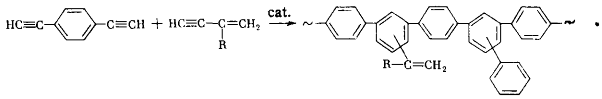
Kern et al.[108] developed a process for obtaining 4-vinylbiphenyl and 1^4-vinyl-*p*-terphenyl by reducing 4-acetylbiphenyl and 1^4-acetyl-*p*-terphenyl with lithium tetrahydroaluminate, and subjecting the resulting α-hydroxyethyl derivatives to liquid-phase dehydration in the presence of methanesulphonyl chloride in pyridine solution:

$$ArCOMe \xrightarrow{LiAlH_4} ArCHOHMe \xrightarrow{MeSO_2Cl} ArCH{=}CH_2 \text{ .}$$

where



Branched oligophenylenes containing double bonds have been obtained[109] by the copolycyclotrimerisation of *p*-diethynylbenzene with alkenylacetylenes—butenyne or methylbutenyne—on the catalysts $[(C_2H_5O)_3P]_4CoBr$, $NiCl_2.2(C_6H_5)_3P.NaBH_4$, $(iso\text{-}C_4H_9)_3Al.TiCl_4$ (Al/Ti = 3):



The content of double bonds and the properties of the oligophenylenes depend primarily on the ratio of *p*-diethynylbenzene to alkenylacetylene in the initial mixture. Thus decrease in the ratio of the former to methylbutenyne tends to increase the solubility and the unsaturation of the oligomers and decrease their molecular mass. Completely benzene-soluble oligophenylenes were obtained at ratios of 1 : 3, when the products had $\overline{M}_n$ = 25 000 and iodine numbers of ~ 195.

Vinylated oligophenylenes obtained from *p*-diethynylbenzene and a vinylacetylene in the molar proportions 1 : 3–9 were solids only partly soluble in benzene and chloroform, probably owing to the ease of cross-linking during isolation and standing in the air. In contrast, ternary copolymers based on *p*-diethynylbenzene, butenyne, and phenylacetylene in the molar proportions 1 : 3 : 3 and 1 : 3 : 1, obtained in the presence of $(iso\text{-}C_4H_9)_3Al.TiCl_4$, dissolved completely in benzene and chloroform; their iodine numbers varied from 130 to 440.

All the alkenylated oligophenylenes were easily hardened at room temperature and on heating with the formation of infusible and insoluble products.

III. POLYMERLIKE REACTIONS OF OLIGO- AND POLYPHENYLENES

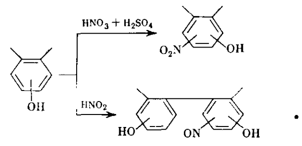
Various functional groups can be introduced into polyphenylenes by treatment with appropriate reagents, whether the polymers had been obtained by dehydrogenation of polycyclohexenes or by oxidative dehydropolycondensation of benzene. Thus Kovačic et al.[110] showed that the action of concentrated sulphuric acid on a *p*-polyphenylene yields a product in which about 60% of the aromatic rings contain sulpho-groups. Sulphonation of *p*-phenylenes with chlorosulphuric acid, oleum, or concentrated sulphuric acid gave sulphonated polymers in which the ratio of carbon to sulphur varied from 6 (one sulphur atom per aromatic ring) to 36 depending on temperature and duration of the reaction[111-113]. Specimens having ratios ≤ 9 dissolved in aqueous acetone and aqueous ethanol.

When a sulphonated polymer was fused with a mixture of sodium and potassium hydroxides 97% of the sulpho-groups were hydrolysed to hydroxy-groups[111]. The resulting hydroxylated polyphenylenes were brittle black products, soluble only in aqueous acetone and aqueous ethanol.

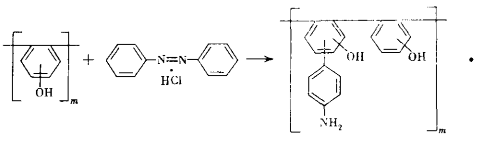
As noted earlier, the oxidative dehydropolycondensation of benzene in the presence of a Lewis acid as catalyst[39,41–44,77] will yield *p*-polyphenylenes having various degrees of halogenation. The hydrogen atoms of the aromatic ring are completely replaced by chlorine when the process is conducted in the presence of gaseous chlorine with $SnCl_2.AlCl_3$ or antimony(V) chloride as catalyst. In the presence of aluminium bromide brominated *p*-polyphenylenes are formed containing on the average ~ 3 bromine atoms per benzene ring[110].

One nitro-group can be introduced into every benzene ring by treating a *p*-polyphenylene with a nitrating mixture (nitric and sulphuric acids)[110]. Aminated polyphenylenes were obtained by reducing the nitro-polymers with hydrazine in the presence of Sn–HCl or $SnCl_2$–HCl in diethylene glycol solution, when conversion of nitro-groups into amino-groups reached 94–100%. The final products contained small quantities of nitro, azoxy, and other functional groups with incomplete reduction, and also because of the occurrence of side-reactions[110].

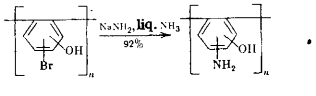
Paushkin et al.[114] used hydroxylated polyphenylenes obtained from dihydric phenols for the preparation of nitro-, nitroso-, and amino-derivatives. Thus treatment with a nitrating mixture (nitric and sulphuric acids) at temperatures not exceeding 10°C introduced a nitro-group into almost every benzene ring. Poly(hydroxynitrophenylenes) were obtained by the action of nitrous acid on a hydroxylated polyphenylene. The general trend of the nitration and nitrosation of these polymers can be represented by the scheme



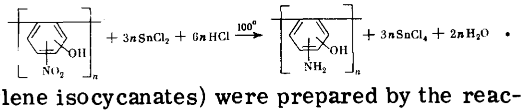
The aminophenylation of hydroxylated polyphenylenes with azobenzene hydrochloride produces polymers that are partly soluble in dimethylformamide and contain one aminophenyl group for approximately two hydroxyphenylene groups[114]:



Polymers completely soluble in dimethylformamide were obtained by the amination of poly(bromohydroxyphenylenes)[114]:



Reduction of poly(hydroxynitrophenylenes) by the action of tin(II) chloride in hydrochloric acid gave up to 70% yields of poly(aminohydroxyphenylenes):



Poly(phenylene isocycanates) were prepared by the reaction of poly(aminohydroxyphenylenes) with chloroform and alkali[114].

The above investigations have shown that the introduction of substituents into hydroxylated polyphenylenes improves their solubility but impairs their thermal stability.

IV. PRACTICAL APPLICATION OF OLIGO- AND POLYPHENYLENES CONTAINING VARIOUS FUNCTIONAL GROUPS

Much experimental information has now accumulated on the preparation and properties of oligophenylenes and polyphenylenes containing functional groups, from which conclusions can be drawn (though still preliminary) on the further development of work on these lines. Fields of practical application of the substituted oligomers and polymers, at present fairly restricted, will undoubtedly expand continuously.

When heated in a melt with alkali, polyphenylenes containing sulpho-groups form polyphenols, which are converted by treatment with formaldehyde into insoluble, infusible cross-linked products[111]. These undergo no loss in weight when heated to 400°C (in nitrogen with ΔT = 2.5 deg min^{-1}), and only at 900°C do the losses amount to 30%. The thermal stability of the products diminishes with increase in the quantity of substituents in the polymer molecule.

A heat-resistant composition was obtained also from a mixture of a chlorinated polyphenylene and a silicone grease[115].

Polyphenylenes having terminal ethynyl groups can be used as binders in polymeric antifriction materials for the production of bearings operating over the temperature range 50–320°C.[116]

Polymers obtained by treating isomeric terphenyls with benzene-*m*-disulphonyl dichloride or benzene-1,3,5-trisulphonyl trichloride at 300–350°C are used for the production of heat-resistant coatings[117]. Such coatings have been obtained also from a mixture of a soluble and a fusible polyphenylene ($\overline{M}_n$ = 500–5000), aromatic sulphonyl halides (e.g. benzene-*m*-disulphonyl dichloride), and an inorganic pigment (titanium dioxide)[118].

Thermosetting polymers of the polyphenylene type are employed as ablative coatings and for the preparation of laminates having high heat resistance[119]. Mixtures of fusible and soluble polyphenylenes were used for these purposes, with 10 wt.% of bishydroxymethylbenzenes as hardeners. $\alpha\omega$-Dibromo-*p*-polyphenylenes are used for the production of heat-resistant coatings[38].

A polymer based on *m*-dibromobenzene, containing *m*-phenylene repeating units, finds application for the manufacture of electrical insulators operating at temperatures of 23–240°C.[120] Hydroxylated *o*-polyphenylenes can be regarded as organic semiconductors[6], having conductivities of 10^{-9}–10^{-8} ohm^{-1} cm^{-1} at 50°C. Alkylated terphenyls are used as heat-transfer agents, regulators, and moderators of neutrons in atomic reactors[62]. Poly(aminohydroxy-*o*-phenylenes) have an inhibiting effect: for example, they prevent the thermal polymerisation of styrene (for up to 1.5 h at 120°C)[114].

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Mass Spectrometry of Quinolizidine Alkaloids

N.S.Vul'fson and V.G.Zaikin

General and specific modes of breakdown on electron bombardment are surveyed for certain simple quinolizidine derivatives, including substances of natural origin, and many quinolizidine alkaloids of the cytisine, sparteine, and matrine series. Mass spectrometry can be used to establish the structure of this class of naturally occurring compounds. A list of 36 references is included.

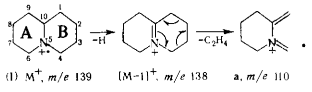
CONTENTS

I. INTRODUCTION

Alkaloids derived from quinolizidine occur widely in the vegetable kingdom. The structures of several dozen natural quinolizidine alkaloids have now been established, and several stereoisomeric compounds, not yet found in Nature, as well as derivatives possessing valuable pharmacological properties, have been prepared from them. Some steroidal alkaloids containing the quinolizidine system, as well as lycopodium alkaloids, can formally be included. However, we have considered it advisable to restrict the present Review to those quinolizidine alkaloids whose degradation on electron bombardment conforms most closely to the rules characteristic of the quinolizidine system. Lycopodium alkaloids and the corresponding steroidal alkaloids are less interesting from this point of view, since the quinolizidine part of the molecule is insufficiently specifically developed in their mass spectra (the modes of decomposition of lycopodium alkaloids on electron bombardment have been summarised in a monograph[1]). The present Review covers mass-spectrometric investigations of quinolizidine and its simple derivatives, including those of natural origin, as well as the more complicated quinolizidine alkaloids belonging to the cytisine, sparteine, and matrine groups.

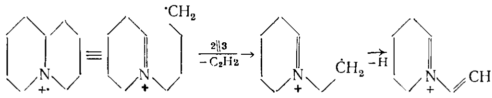
II. QUINOLIZIDINE AND ITS SIMPLE DERIVATIVES

Detailed reviews have appeared on the behaviour under electron bombardment of quinolizidine itself (I) and its deutero-analogues[2-5]. The maximum peak in the mass spectrum of (I) corresponds to the $[M-1]^+$ ion, the peak due to the molecular ion being only about half as intense[4]. Analysis of the mass spectra of the analogues labelled with deuterium at the 1,4 and 2,10 positions showed that the above ion is formed by preferential elimination of the hydrogen atom from the $C_{(10)}$ carbon atom, whereas at most 11% of the hydrogen is lost from $C_{(4)}$ and $C_{(6)}$ adjacent to the nitrogen atom[5]. Further breakdown of the $[M-1]^+$ ion, on the pattern of a retrodiene reaction (RDR), yields an ion (a) having $m/e = 110$:



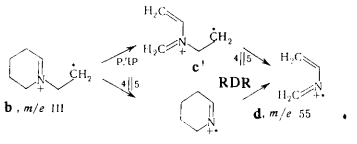
(I) $M^{+\cdot}$, m/e 139 $[M-1]^+$, m/e 138 a, m/e 110

It is supposed furthermore that this 110 ion may be formed from the molecular ion by successive rupture of the $C_{(10)}-C_{(1)}$ and $C_{(2)}-C_{(3)}$ bonds with elimination of an ethylene molecule and formation of an m/e 111 ion (b), which then loses a hydrogen atom. The 110 ion will then have the structure a'[4]:



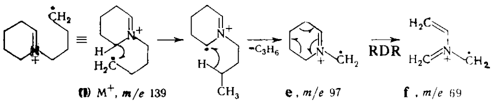
(I) M^+, m/e 139 b, m/e 111 a', m/e 110

Nor can it be excluded that (a') may be formed from the $[M-1]^+$ ion as a result of elimination of an ethylene molecule with rupture of the above two bonds accompanied by migration of a hydrogen atom from $C_{(4)}$ to $C_{(10)}$. Elimination of an ethylene molecule from ion b by rupture of $C_{(4)}-C_{(5)}$ or a retrodiene type of breakdown in ring *A* yields ions having m/e 83 (c or c'), which then lose another ethylene molecule to give the ion d with m/e 55:



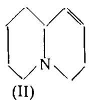
c, m/e 83

The characteristic ion e with m/e 97 is formed directly from the molecular ion (I). It was shown by means of deuterated analogues[3] that formation of this ion (e) is due to elimination of the $C_{(1)-(3)}$ atoms accompanied by countermigration of hydrogen atoms:

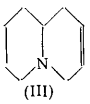


(I) M^+, m/e 139 e, m/e 97 f, m/e 69

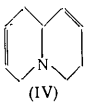
The introduction of double bonds into the quinolizidine molecule results in appreciable simplification of the mass spectrum[6]. The peaks due to molecular and $[M-1]^+$ ions are very intense in the spectra of Δ^1-, Δ^2-, and $\Delta^{1,7}$-dehydroquinolizidines



(II)



(III)



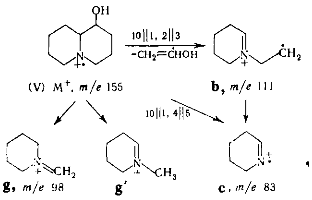
(IV)

[with (II) and (IV) the latter ions are the most intense in the spectrum]. The c ion, formed by a retrodiene type of breakdown in the B ring and then decomposing to the ion d, has the maximum intensity in the spectrum of (III).

The spectra of (II) and (IV) are characterised by unsaturated analogues of c ions with *m/e* 80 and 81. That of (II) also contains a peak due to an unsaturated analogue of the ion a′ with *m/e* 108.

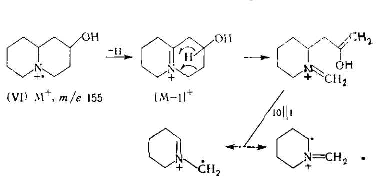
The introduction of a hydroxy-group into the quinolizidine molecule in principle leaves unchanged the modes of breakdown of the main skeleton under electron bombardment. However, the intensities with which certain processes occur depend both on the presence of such a group and on its position.

The peaks of molecular and $[M - 1]^+$ ions in the mass spectra[5] of 1-, 2-, and 3-hydroxyquinolizidines (V)-(VII) are quite intense; they are more intense with (VI) and (VII) than with (V), and in these two cases the $[M - 1]^+$ ions are more intense than the molecular ions. The main peaks in the spectra of (V) and (VII) are due to the ions c with *m/e* 83. This ion may be formed from (V) either directly from the molecular ion by rupture of $C_{(10)}-C_{(1)}$ and $C_{(4)}-C_{(5)}$ bonds or from the b ion with *m/e* 111 by loss of an ethylene molecule in the rupture of the $C_{(4)}-C_{(5)}$ bond:



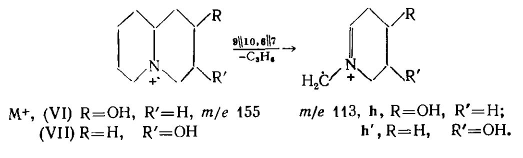
In the case of (VII) the ion c is formed only bh the first route[5].

Analysis of the mass spectra of deuterated analogues showed that the next most intense peak in the spectrum of (V) with *m/e* 98 is due to the isomeric ions g and g′, formed directly from the molecular ion by rupture of the $C_{(10)}-C_{(1)}$ and $C_{(3)}-C_{(4)}$ bonds with migration of a hydrogen atom to the charged particle. The most intense peak in the spectrum of (VI) is an ion having *m/e* 97 (e or e′):

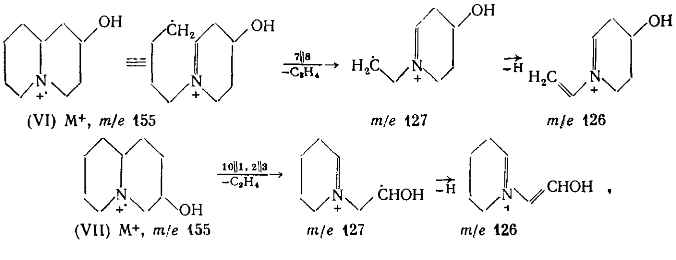


The peaks due to ions a–c are moderately intense in the spectrum of (VI). Whereas the peaks due to $[M - OH]^+$ ions are relatively weak in the spectra of (V) and (VII), the corresponding peak in the spectrum of (VI) is similar in intensity to that due to the molecular ion.

A peculiarity of the breakdown of the hydroxy-derivatives (VI) and (VII) under electron bombardment is the formation of several oxygen-containing fragments almost completely absent from the spectrum of (V). Both the former compounds are characterised by fairly intense peaks due to ions having *m/e* 113 (h and h′ respectively), resulting from rupture of $C_{(6)}-C_{(7)}$ and $C_{(9)}-C_{(10)}$ bonds with localisation of the charge on the oxygen-containing fragment:



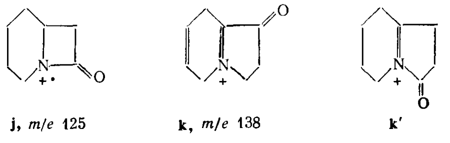
A different pattern obtains in the formation of ions with *m/e* 126 and 127, for analysis of the mass spectra of deuterated analogues of (VI) and (VII) indicates different mechanisms of formation and hence different structures:



A distinguishing feature of the mass spectrum of (VII) is the quite considerable intensity of peaks due to $[c + 1]^+$ and g ions with *m/e* 84 and 98 respectively. The spectra of all the above compounds contain not very intense peaks due to $[e - 1]^+$ ions with *m/e* 96.

Introduction of a keto-group into the quinolizidine molecule has a still more marked effect on the character of the mass spectrum. Spectra have been described for the derivatives (VIII)-(XI) with this group in positions 1-4 [4,7] and their deuterated analogues. They all differ significantly in the intensity of the peak due to the molecular ion: with (IX) and (XI) these peaks are the most intense, with (X) the intensity is ~60%, and with (VIII) only ~30%. Although a hydrogen atom is eliminated from the molecular ion in all cases, this process is less characteristic of the ketones (VIII)-(XI) than of the previous examples. The position of the keto-group has a very significant influence on the breakdown of the molecular ion, although in many cases the resulting ions have the same structure as previously. Successive elimination of a carbon monoxide molecule and a hydrogen atom with formation of ions having *m/e* 125 and 124 is most characteristic of the molecular ions of (VIII) and (X), and is confirmed by the spectra of the deuterated analogues and by the presence of the corresponding metastable peaks in the spectra[4]. In both cases different structures were ascribed to these ions, which the Reviewers regard as unsound.

Peaks due to ions with *m/e* 125 and 124 are completely absent from the mass spectrum of (IX) [4], whereas the 125 peak is present in the spectrum of (XI); according to a high-resolution mass spectrum, however, it is due to elimination of an ethylene molecule—not of carbon monoxide—and has the structure j.[7] A distinguishing feature of these ketones (IX) and (XI) is the elimination of a methyl group from the molecular ions with formation of ions having *m/e* 138 (k and k′).[4,7]



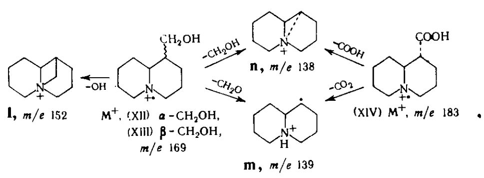
The spectra of all the ketones examined contain peaks due to ions of the previous types a and c–g; the b ion is apparent only in the spectrum of (IX). The high-resolution mass spectrum indicates that the 97 peak in the case of (X) is composite, representing not only ions e and e′ but also ions of composition C_7H_{13} and C_6H_9O.

It must be emphasised that the above ions of types a–g are in general present in the mass spectra of all quinolizidine alkaloids, their intensity varying with the type of fusion of the rings and with the nature and position of substituents.

III. QUINOLIZIDINE ALKALOIDS

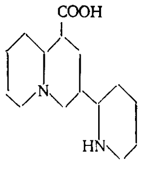
1. Simple Alkaloids

The mass spectra of the simplest quinolizidine alkaloids—lupinine (XII), isolupinine (XIII), and lupininic acid (XIV)—were described by Spiteller et al.[8] as long ago as 1964. The spectra of the epimeric alcohols (XII) and (XIII) differ little. The peaks of molecular and $[M - 1]^+$ ions are fairly intense. These compounds undergo not only the above modes of decomposition giving the ions a–g but also fragmentation of the hydroxymethyl group, with elimination of a hydroxyl radical or a formaldehyde molecule (giving the ions *l* and m with *m/e* 152 and 139 respectively), and loss of a hydroxymethyl radical yields the ion n with *m/e* 138:

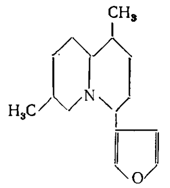


The peaks of *l* and n ions are among the most intense in the spectrum. The maximum peaks in the spectra of (XII) and (XIII) are produced by c and *l* ions respectively. The c peak predominates also in the spectrum of the acid (XIV), about threefold the intensity of the molecular ion. Loss of carboxyl and of carbon dioxide yields respectively n and m ions.

The mass spectra of α-epilupininic acid, its ethyl ester, amide, piperidide, and morpholide, and also aphyllinic acid (XV), its amide, methyl ester, and several other derivatives have been described[9]. Whereas the molecular ion of α-epilupininic acid breaks down on electron bombardment mainly similarly to (XIV), aphyllinic acid (XV) exhibits special trends resulting from the presence of a piperidine residue in its molecule. The principal feature of the spectrum of (XV) is the peak of the *m/e* 84 ion, which, though corresponding in structure to the $[c + 1]^+$ ion, is nevertheless due entirely to localisation of charge on the piperidyl residue. The remaining peaks in the spectrum of (XV) are far less intense than the 84 peak. Among fragments formed at the expense of the quinolizidine ring the most clearly evident are the a, e, and g ions. The $[M - 84]^+$ and $[M - 83]^+$ ion peaks owe their appearance to detachment of the piperidyl residue with localisation of the charge on the quinolizidine moiety. Several other peaks in the spectrum of (XV) may be explained by preliminary cyclisation of the molecular ion by elimination of a water molecule from the carboxyl and the secondary amino-group with formation of the polyheterocyclic structure of aphylline (see below).

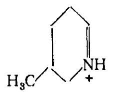


(XV)

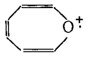


(XVI)

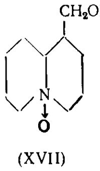
In the mass spectrum of deoxynupharidine (XVI)[10] the moderately intense peak due to the molecular ion is accompanied by the strongest peak at *m/e* 98, due to a homologue of the $[c + 1]^+$ ion formed by rupture of the $C_{(10)}-C_{(1)}$ and $C_{(4)}-C_{(5)}$ bonds. When the same bonds are broken but with localisation of the charge on the other moiety and migration of a hydrogen atom from the charged particle, an ion having *m/e* 136 is formed. A third, fairly intense peak at 94 is due to the oxatropylium radical-ion resulting from localisation of charge on the furan substituent.



m/e 98



m/e 94



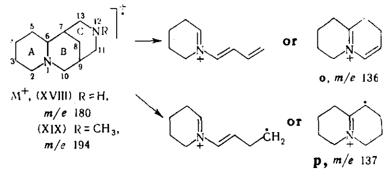
(XVII)

In concluding this subsection we must mention that mass spectra have been described also for two lupinine *N*-oxides (XVII) epimeric at the nitrogen atom[11]. Unfortunately, one of the spectra clearly corresponds to an impure compound, so that it is impossible to assess the effect of the stereochemistry on the decomposition of the molecular ions of these epimers on electric bombardment. From the spectrum of the pure epimer, however, it appears that the main path involves the successive elimination of a hydroxy-group and an oxygen atom from the molecular ion. The presence of an ion peak at 138 is probably due to elimination of a formaldehyde molecule from the $[M - OH]^+$ ion.

2. Cytisine Series

Ring *A* of the parent compound of this group of quinolizidine alkaloids (cytisine) has an α-pyridone structure, which has a significant influence on the general pattern of decomposition of this compound under electron bombardment. The successive hydrogenation and reduction of cytisine yields tetrahydrocytisine and deoxytetrahydrocytisine. The latter contains the quinolizidine structure in "pure form", so we considered it advisable to begin our survey of this group of alkaloids at this compound, and then pass to tetrahydrocytisine and cytisine, in order to trace the influence of functional groups introduced into ring *A* on the type of breakdown under conditions of mass spectrometry.

The mass spectra of deoxytetrahydrocytisine (XVIII) and its *N*-methyl derivative (XIX)[8] contain fairly intense peaks of molecular ions. The maximum peaks in the two spectra are due to g and g′ ions respectively, while the e peaks are considerably less intense. Both these ions result almost entirely from rupture of $C_{(6)}-C_{(7)}$ and $C_{(9)}-C_{(10)}$ bonds with localisation of charge on the *A* ring. This is confirmed by the constancy of the peaks on passing from (XVIII) to (XIX) and the displacement of both peaks by 2 amu in the spectrum of 2,2-dideuterated (XVIII). Among fragments noted earlier as characterising the quinolizidine system, peaks of [e − 1] ions (also formed from ring *A*) and a ions are present in the spectra of (XVIII) and (XIX). Breakdown of the molecular ion of (XVIII) involves ejection of the nitrogen atom at position 12 as amino or methylamino. With (XIX) the peak of the $[M - CH_3NH]^+$ ion with *m/e* 164 is accompanied by the $[M - (CH_3)_2N]^+$ peak at 150 and the peak of the $[M - 15]^+$ ion. The spectra of (XVIII) and (XIX) are characterised by pairs of peaks due to ions having *m/e* 136 (o) and 137 (p)



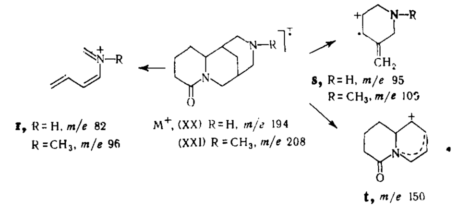
M⁺, (XVIII) R = H, *m/e* 180
(XIX) R = CH_3, *m/e* 194

o, *m/e* 136

p, *m/e* 137

for whose formation several complicated rearrangement mechanisms have been suggested[8]. As will be seen later, o and p ions are characteristic also of quinolizidine alkaloids.

The presence of the lactam carbonyl in the *A* ring of tetrahydrocytisine (XX) and its *N*-methyl derivative (XXI) has a significant influence on the type of breakdown under electron bombardment[12]. The principal peaks in their mass spectra correspond to $[M - 112]^+$ and $[M - 99]^+$ ions. They are formed by complicated rearrangements involving destruction of the polyheterocyclic system, and have been ascribed the structures r and s; elimination of the elements of ring *C* from (XX) and (XXI) yields an *m/e* 150 ion (t):



r, R = H, *m/e* 82
R = CH_3, *m/e* 96

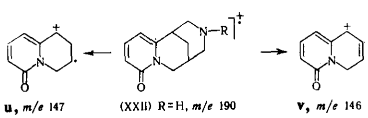
M⁺, (XX) R = H, *m/e* 194
(XXI) R = CH_3, *m/e* 208

s, R = H, *m/e* 95
R = CH_3, *m/e* 109

t, *m/e* 150

However, elimination of $CH_3NH\cdot$ and $(CH_3)_2NH\cdot$ radicals from the molecular ions of these alkaloids is not observed.

The molecular ions of cytisine (XXII) and *N*-methylcytisine (XXIII)—alkaloids containing an aromatised *A* ring—are very stable. The spectrum of (XXII) contains not only the peak due to the $[M - CH_3NH]^+$ ion but also a pair of peaks (equal in intensity to the molecular ion) having *m/e* 147 and 146, corresponding to the ions u and v formed by elimination of the elements of ring *C*:



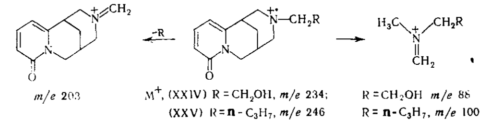
u, *m/e* 147

(XXII) R = H, *m/e* 190
(XXIII) R = CH_3, *m/e* 204

v, *m/e* 146

Unexpectedly, the spectrum of (XXIII) differs markedly from that of (XXII). Thus the u peak is almost completely absent, and the $(CH_3)_2N^+:CH_2$ ion with *m/e* 58 produces the maximum peak in the spectrum. The corresponding ion with *m/e* 44 from (XXII) is very weak. This effect is attributed to the different abilities of the $N_{(12)}$ atoms in (XXII) and (XXIII) to localise the positive charge. The spectra of (XXII) and (XXIII) also contain peaks at *m/e* 160 due to $[M - CH_3NH]^+$ and $[M - (CH_3)_2N]^+$ ions respectively.

In several cases the cytisine group of alkaloids can be distinguished from the sparteine and matridine groups simply on the basis of molecular weight, since the first group do not contain the *D* ring. Although several dimeric cytisine alkaloids and those containing substituents in the *C* ring are now known, with consequently considerably higher molecular weights, the problem can still be solved quite simply, since the substituent is easily detached on electron bombardment, yielding one of the maximum ion peaks in the spectrum, and dimeric molecules are broken "in half", so that the low-molecular regions resemble the spectra of the corresponding monomeric derivatives. For example, the main peaks in the spectra of *N*-hydroxyethylcytisine (XXIV)[13] and *N*-n-butylcytisine (XXV)[14] represent ions with *m/e* 203, corresponding to detachment of part of the $N_{(12)}$-substituent; they are accompanied by peaks peculiar to cytisine, and the 58 peak characteristic of *N*-methylcytisine is replaced by peaks displaced to *m/e* 88 and 100:

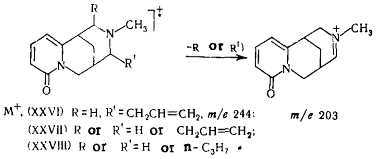


m/e 203

M⁺, (XXIV) R = CH_2OH, *m/e* 234;
(XXV) R = n-C_3H_7, *m/e* 246

R = CH_2OH *m/e* 88
R = n-C_3H_7, *m/e* 100

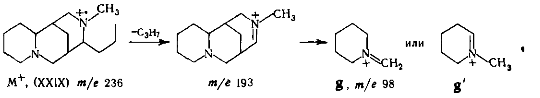
Alkyl groups located in the α-position relative to the nitrogen atom in the *C* ring of cytisine alkaloids are readily split off, so that the mass spectra of tinctorine (XXVI)[15], the perhaps identical alteramine (XXVII)[14], and also dihydroalteramine (XXVIII)[14] contain peaks of ions having *m/e* 203 together with those of ions characteristic of breakdown of the cytisine ring system:



M⁺, (XXVI) R = H, R' = $CH_2CH{=}CH_2$, *m/e* 244;
(XXVII) R or R' = H or $CH_2CH{=}CH_2$;
(XXVIII) R or R' = H or n-C_3H_7 .

m/e 203

Similarly, the most intense peak in the spectrum of hexahydroalteramine (XXIX)[14] corresponds to the $[M - n\text{-}C_3H_7]^+$ ion, which then breaks down into a g or g′ ion:



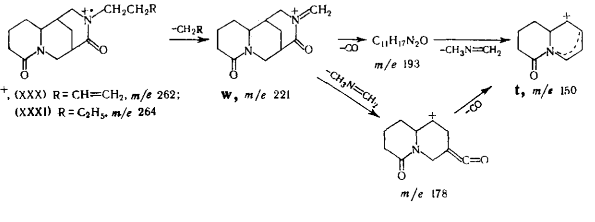
M⁺, (XXIX) *m/e* 236

m/e 193

g, *m/e* 98

g′

In tetrahydro-11-oxorhombifoline (XXX) and its dihydro-derivative (XXXI) the *C* ring contains a lactam carbonyl as well as an alkyl group[16]. Nevertheless, the maximum peak in the spectrum of (XXX) is due to an ion formed by detachment of part of the alkyl substituent. This ion with *m/e* 221 (w) then loses carbon monoxide and $CH_3N:CH_2$, being converted into ions 193 and 178, which in turn eliminate $CH_3N:CH_2$ and CO respectively to form the ion t (*m/e* 150):



M⁺, (XXX) R = $CH{=}CH_2$, *m/e* 262;
(XXXI) R = C_2H_5, *m/e* 264

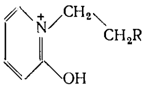
w, *m/e* 221

m/e 193

t, *m/e* 150

m/e 178

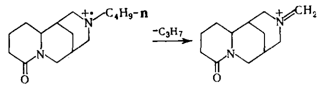
However, analysis of the mass spectrum of the 3,3-dideutero-analogue of (XXX) showed that the 150 peak is only partly displaced to 152, and is therefore composite, being due both to the t ion and to an ion t′ formed by rupture of bonds in the *B* ring with preservation of the *C* ring:



t′, R=CH=CH₂, *m/e* 150;

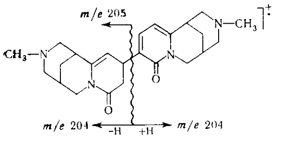
R=C₂H₅, *m/e* 152.

Breakdown of the molecular ion (XXXI) is essentially analogous to that of (XXX), differing only in containing a peak at 152 due to the t′ ion. The main peak in the mass spectrum of hexahydrorhombifoline (XXXII), briefly described in Ref. 17, is also due to the deoxy-analogue of the w ion with *m/e* 207, whose breakdown leads to ions at 138, 112, and 58:

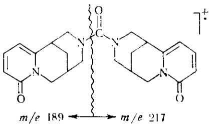


M⁺. (XXXII) *m/e* 250 *m/e* 207

The spectrum of the dimeric cytisine alkaloid—dimethamine (XXXIII) [18]—contains a very small peak of the molecular ion and intense ion peaks at 205 and 204, due to breakage of the molecule "in half" (accompanied by migration of a hydrogen atom to or from the charged particle):



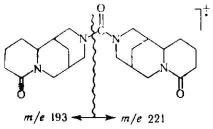
M⁺. (XXXIII) *m/e* 408



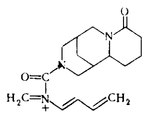
M⁺. (XXXIV) *m/e* 406

The spectrum of (XXXIII) also contains ion peaks typical of *N*-methylcytisine—at 160 [M^{+}_{cyt} − $(CH_3)_2N$], 146 (v), and the maximum at 58 $(CH_3)_2N^+$: CH_2—see above.

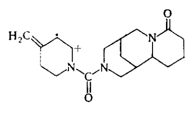
Argentine (XXXIV) belongs to a different type of dimeric cytisine alkaloids. Its mass spectrum [19,20] contains a fairly intense peak of the molecular ion and most intense peaks at 189 and 217 due to ions formed by rupture of carbon–nitrogen bonds around the central carbonyl group. Analogous breakages lead to ions with *m/e* 193 and 221, which give intense peaks in the spectrum of octahydroargentine (XXXV). [19,20] Ions at 302 and 315 are diagnostically important in the latter spectrum, for they are characteristic of the tetrahydrocytisine skeleton and are more complicated analogues of ions r and k respectively:



M⁺ (XXXV) *m/e* 414



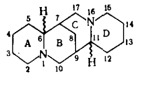
m/e 302



m/e 315

3. Sparteine Series

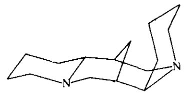
The simplest naturally occurring member of this series of alkaloids, which contains no functional group, is sparteine itself (XXXVI*a*), whose molecule is formed by two quinolizidine residues with a bridge between them



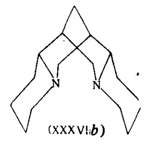
(XXXVI*a*) 6β-H, 11α-H
(XXXVI*b*) 6β-H, 11β-H
(XXXVI*c*) 6α-H, 11α-H .

Two other stereoisomers are known—α-isosparteine (XXXVI*b*) and β-isosparteine (XXXVI*c*)—as well as its *d*-enantiomer, pachycarpine (XXXVII). In principle molecular ions of these compounds break down in the same ways, although certain quantitative differences exist between the mass spectra of (XXXVI*a*) and (XXXVI*b*)[8], in particular in the ratio of the peaks of ions having *m/e* 98 and 137. The mass spectra of (XXXVI*a*) and (XXXVII) should be absolutely identical, since as optical enantiomers they have the same internal energy. Nevertheless, a difference in intensity between individual peaks (measured as percentages of the total ion current) was reported [17] between the spectra of (XXXVI*a*) and (XXXVII) obtained under the same conditions. To the Reviewers this appears strange; the attempt [17] to explain the difference by the possibility of interaction between the electric field and the molecule and by the spatial orientation of the molecule before ionisation does not stand up to criticism.

The main peaks in the mass spectra of (XXXVI*a*, *b*) and (XXXVII) [8,21] are due to the molecular, g, and p ions (the latter two with *m/e* 98 and 137 respectively); the peaks due to the ions c + 1, e, and o (84, 97, and 136) are of moderate intensity. Because of the apparent symmetry of the molecules (XXXVI*a*–*c*) it might be assumed that the ions c, c + 1, e, e − 1, g, o, and p are equally likely to be formed by rupture of bonds in ring *B* or in ring *C*, i.e. that the first five ions may contain ring *A* or *D* to equal extents, and that the last two ions may equally contain rings *A* + *B* or *C* + *D*. With sparteine (XXXVI*a*), however, in which the fusion of rings *A* and *B* is *trans*, whereas that of *C* and *D* is *cis*, only e and o ions are equally likely to contain an *A* or a *D* ring, and hence *A* + *B* or *C* + *D*, as Spiteller et al. showed [8] in experiments using a deuterium label. The ions c + 1 and g are 85–90% formed from the *A* ring, whereas p ions result from the *A* + *B* rings. The Reviewers have obtained similar results [21] from a comparison of the mass spectra of (XXXVI*a*) and its 3,3-dideutero-analogue, as well as by analysing the spectra of 13- and 14-hydroxysparteines [3,8], in which the 98 and 137 peaks have been only 85% shifted to *m/e* 114 and 153 respectively. The effect is explained by Spiteller et al. [8] firstly by the different degrees of stress in rings *B* and *C* in (XXXVI*a*) resulting from the difference in the stereochemistry of their fusion with rings *A* and *D*, and secondly by the different tendencies to migrate, resulting from the stereochemistry of the molecule, of hydrogen atoms involved in forming these rearranging ions.



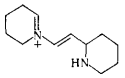
(XXXVI*a*)

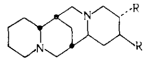


(XXXVI*b*)

The α-isosparteine molecule (XXXVI*b*), in which both *A*–*B* and *C*–*D* ring fusions are *trans*, is symmetrical, in contrast to the sparteine molecule. Therefore equally probable formation of g and p ions (*m/e* 98 and 137) may be expected from ring *A* or *D* and from *A* + *B* or *C* + *D* respectively, since in this case rings *B* and *C* are energetically equivalent. This suggestion was tested by preparing[20] the 3,4,5,6-tetradeutero-analogue of α-isosparteine, whose mass spectrum showed that the peak of the g ions was at least half displaced by 4 amu (to *m/e* 102). The p ion peak is accompanied by equally strong peaks at *m/e* 138, 139, and 140. Since the 137 ion undergoes rearrangement, and the displacement of the peak suggests that hydrogen atoms from the *A* ring are involved in its formation, it may be concluded that with α-isosparteine, in contrast to sparteine itself, the g and p ions are equally formed by charge localisation on fragments containing both *A* and *A* + *B* and *D* and *C* + *D* rings.

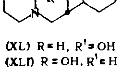
Analysis of the mass spectrum of the 3,3-dideutero-analogue of sparteine has shown[20,21] that formation of the ion t with *m/e* 150 is independent of the stereochemistry of *A*–*B* and *C*–*D* ring fusion and is due to the equally probable localisation of charge on fragments containing the rings *A* + *B* and *C* + *D*. The diagnostically most significant feature of the mass spectra of sparteine and its stereoisomers, enabling them to be distinguished from the isomeric matridine derivatives (see below), is the presence of fairly intense $[M - 41]^+$ ion peaks having *m/e* 193. This ion is probably formed from the molecular ion of sparteine by elimination of a cyclopropyl or an allyl radical on the rupture of bonds in rings *B* and *C*, which is supported by the mass spectra of the corresponding deutero-analogues[8,20,21]. In the view of Spiteller et al.[3] this ion has the structure x.

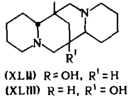

x, *m/e* 193

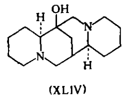

(XXXVIII) R = OH, R' = H
(XXXIX) R = H, R' = OH

The paper by these workers[3] was devoted mainly to a mass-spectrometric study of hydroxy-derivatives of sparteine. The paths along which the molecular ions of 13-hydroxysparteine (XXXVIII)[8] and its 14*e*-isomer (XXXIX)[3] decompose are analogous to those described for sparteine itself with, as already noted above, the peaks of g and p ions displaced by 16 amu owing to charge localisation on the oxygen-containing moiety. In both cases the $[M - 41]^+$ ion peaks exhibit appreciable intensity. The presence of the hydroxy-group in (XXXVIII) and (XXXIX) is shown in the spectrum of the former by the appearance of an $[M - 17]^+$ ion peak, and in that of the latter by a pair of peaks due to $[M - 17]^+$ and $[M - 18]^+$ ions.

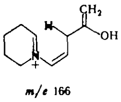
The mass spectra of 8-hydroxy- and 8-epihydroxysparteine (XL) and (XLI) differ fairly strongly from those of the preceding compounds. Thus peaks of p ions (*m/e* 137) are regularly absent, but are replaced by some of the most intense peaks of the hydroxylated analogues of p ions (*m/e* 153). The spectra also contain fairly intense peaks of o ions (136), obviously formed from these analogues by ejection of the hydroxyl radical. Among ions typical of the quinolizidine system and containing no hydroxy-group, a, e, and g are present in the spectra of (XL) and (XLI). The peaks of $[M - 41]^+$ ions have been replaced by [M – 57] ion peaks: i.e. formation of these ions involves loss of a hydroxy-group in neutral species, which provides additional conformation of the origin of the x ion (*m/e* 193) in the case of sparteine. The hydroxyl is eliminated from the molecular ions of (XL) and (XLI).

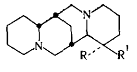

(XL) R = H, R' = OH
(XLI) R = OH, R' = H

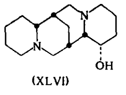

(XLII) R = OH, R' = H
(XLIII) R = H, R' = OH


(XLIV)

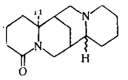
The decomposition paths of 7- and 9-hydroxysparteines (XLII) and (XLIII) and also of 7-hydroxy-β-isosparteine (XLIV) are fairly similar and somewhat recall those for (XL) and (XLI). In all cases the g ion peaks are dominant. In contrast to the preceding compounds, peaks due to o ions (*m/e* 136) are absent from (XLII)–(XLIV), but peaks appear at 166, due to ions formed by elimination of the elements of the *D* ring[3]. A peculiarity of these mass spectra is the presence of $[M - 57]^+$ together with $[M - 41]^+$ ion peaks.

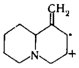

m/e 166

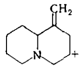

(XLV) R' = OH, R = H
(XLVa) R' = H, R = OH

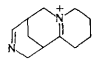

(XLVI)

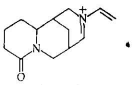
In contrast to all the above hydroxysparteines, the molecular ions of retamine (XLV), epiretamine (XLV*a*), and 12*e*-hydroxy-α-isosparteine (XLVI) are fairly easily dehydrated, with the $[M - H_2O]^+$ ion providing one of the main peaks in the spectrum of (XLV*a*). Explaining the increased intensity of the peak of the dehydration ion in the spectrum of epiretamine in comparison with that of retamine (containing respectively an equatorial and an axial hydroxyl), Spiteller et al.[3] suggest that the *D* ring in the former compound can pass into the boat form and thus ensure easier detachment of a water molecule by 1,4-diaxial elimination. The main peak in the spectra of all three compounds corresponds to the g ion, and the spectra also contain several peaks due to the decompositon of $[M - H_2O]^+$. A peculiarity of the spectra of these compounds is that the $[M - 41]^+$ have been replaced by the $[M - 43]^+$ ion peaks


(XLVII) α-H
(XLVIIa) β-H


y, *m/e* 149

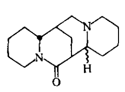

y + 1, *m/e* 150


m/e 177

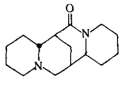

[M – 29]

In the spectra of all the oxosparteines the peaks of the molecular ions are of moderate intensity. The spectra of lupanine (XLVII)[12] and α-isolupanine (XLVII*a*)[21] are almost identical. The peaks of c + 1, e, and g ions, which retain the *D* ring, are weak; the dominating peaks are due to o ions (*m/e* 136), formed directly from the molecular ions, as indicated by the presence of the corresponding metastable peaks. The charge is localised on the fragment containing the *C* + *D* ring system. Cleavage of the *B* ring yields in both cases ions having *m/e* 149 and 150 (y and y + 1). The composition of the latter ion is supported only by a slight shift of the corresponding peak to 152 in the spectrum of the 3,3-dideutero-analogue of α-isolupanine[21]. In the range of mass numbers from *m/e* 150 to the molecular ion the spectra of both compounds contain low-intensity peaks, among which the most interesting are at 177, due to $C_{11}H_{17}N_2$ ions according to the high-resolution mass spectrum of (XLVII*a*), and also $[M - 29]^+$ ion peaks due to elimination of an ethyl radical from the *D* ring. Thus here, as with tetrahydrocytisine, the presence of a lactam carbonyl in the *A* ring does not favour charge localisation on ions containing this ring.

If the lactam carbonyl is located in the *B* ring, as in aphylline (XLVIII) and epiaphylline (XLVIII*a*)[12], the peaks of t and y ions are much less intense, while the peaks of o ions remain the most intense. The $[M - CO]^+$ ion peaks exhibit considerable intensity, and peaks appear at 191 and 192 owing to elimination of CH_3CH_2CO and CH_2CH_2CO particles from rings *B* and *C* of the molecular ions.



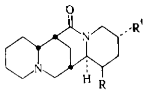
(XLVIII) α-H
(XLVIIIa) β-H



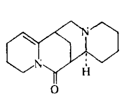
(XLIX)

In the case of 17-oxosparteine (XLIX) [12] the main peak corresponds to the e ion (*m/e* 97), and is accompanied by strongly intensified a and g peaks. The presence of a fairly intense $[M - CO]^+$ ion peak and an appreciable pair of peaks at 191 and 192 is characteristic of the spectrum of (XLIX). In contrast to lupanine, the spectra of (XLVIII), (XLVIII*a*), and (XLIX) contain y + 1 ion peaks that are considerably more intense than the y ion peaks (at 150 and 149).

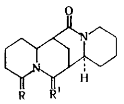
Introduction of a 14*e*-hydroxy-group into the 17-oxosparteine molecule (L) [12] hardly affects the pattern of decomposition under electron bombardment. The main peaks are still those of e and g ions, and an $[M - CO]^+$ ion peak is also observed, but ejection of the hydroxyl as a radical or a water molecule is completely absent. In the case of "17-oxoretamine" (12*a*--hydroxy-17-oxosparteine) (LI) [12] the $[M - 17]^+$, e, and g ion peaks are dominant, while peaks due to other ions are weak.



(L) R = H, R' = OH
(LI) R = OH, R' = H

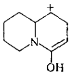


(LII)

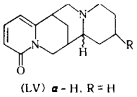


(LIII) R = O, R' = H₂
(LIV) R = H₂, R' = O

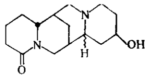
The presence of a double bond in the *A* ring of aphyllidine (LII) [12] prevents cleavage of bonds in the *B* ring, but the *C* ring opens fairly easily. The main peaks in the spectrum of (LII) are therefore due to e and g ions. In the spectrum of the dilactam—17-oxolupanine (LIII) [12]—on the other hand, the main peak is due to the t ion (*m/e* 150), which was regarded as containing *A* and *B* rings. The same peak predominates also in the spectrum of 10,17-dioxosparteine (LIV) [12], but is accompanied by an intense peak at 152, possibly due to an ion having the structure **z**.



z, *m/e* 152

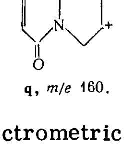


(LV) α-H, R = H
(LV*a*) β-H, R = H
(LVI) R = OH



(LVII)

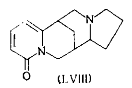
Two naturally occurring stereoisomers—anagyrine (LV) and *d*-thermopsine (LV*a*)—are sparteine alkaloids containing an aromatic ring *A*. Their mass spectra differ little [8,20,21], although peaks of individual ions may vary slightly in relative intensity. The strongest peaks in both spectra are due to g ions (*m/e* 98); they also contain peaks of o ions containing the *C* + *D* ring system, v ions, and q ions (*m/e* 136, 146, and 160 respectively).



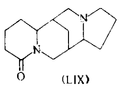
q, *m/e* 160.

Analysis of mass-spectrometric results proved that the alkaloid argentamine (LVI) [22] was a hydroxy-derivative of thermopsine. Its spectrum contained an intense peak of the molecular ion with *m/e* 260 which exceeds the molecular weight of anagyrine (LV) and *d*-thermopsine (LV*a*) by 16 amu, although the breakdown of molecular ions of all three compounds follows closely similar routes. Only the peaks of ions that in the cases of (LV) and (LV*a*) definitely contain the *D* ring move up by 16 amu on passing to the compound (LVI). Thus the peaks of g and o are displaced to *m/e* 114 and 152 respectively, whereas the peaks of v and q ions, which do not contain the *D* ring, remain fixed.

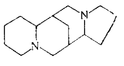
A similar situation is found on comparing the mass spectra of tetrahydroargentamine (LVII) and lupanine (XLVII) or α-isolupanine (XLVII*a*). The most intense peaks in the spectra of the latter two compounds—of o and y ions, containing *C* and *D* rings—are completely displaced by 16 amu to *m/e* 152 and 165 respectively on passing to (LVII). These results prove that the alkaloids (LVI) contains a hydroxy-group in the *D* ring, whose position at $C_{(13)}$ follows from the complete identity of the mass spectra of deoxytetrahydroargentamine and 13-hydroxysparteine (XXXVIII). [8]



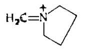
(LVIII)



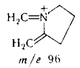
(LIX)



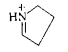
(LX)



m/e 84

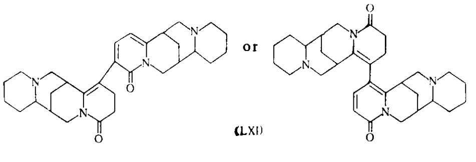


m/e 96



m/e 70

Interesting work was undertaken by Yunusov et al. [23] on the mass spectra of leontidine (LVIII) and its tetrahydro- and deoxytetrahydro-derivatives (LIX) and (LX), which contain a five-membered instead of a six-membered *D* ring. In the spectrum of (LVIII) the ions containing *A* and *B* rings (v and q) have the same mass numbers as in the spectrum of anagyrine (LV), whereas ions of types a and g, containing a five-membered ring, have *m/e* 96 and 84 respectively, with the latter the maximum peak in the spectrum (as with anagyrine, when it has *m/e* 98). A similar situation obtained in the spectrum of (LIX), in which the peak of the t ion (*m/e* 150) was accompanied by a peak at 136 corresponding to an analogue of the y + 1 ion with a five-membered ring. In the spectrum of deoxytetrahydroleontidine (LX) the ions with *m/e* 84, 98, and 137, containing *A* and *B* rings, correspond to c + 1, g, and p ions, whereas the ions at 96 and 70 are analogues of a and c + 1 ions resulting from a five-membered *D* ring.



(LXI)

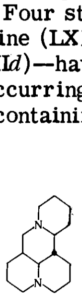
In concluding this subsection we must mention results[24] for the mass spectrum of the dimeric sparteine alkaloid diteramine (LXI), which contains a small peak of the molecular ion, a peak of an ion corresponding to the molecular ion of thermopsine with *m/e* 244, and also peaks of v and q ions. The g ion peak is the maximum, which is typical of the spectra of thermopsine and anagyrine.

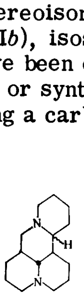
4. Matrine Series.

Alkaloids of this type differ from the sparteine series in the mode of fusion of the two quinolizidine systems. Unsubstituted matrine alkaloids have not yet been discovered in Nature, in contrast to the situation in the sparteine series. Isomers of sparteine in the matrine series have been obtained only artificially, by reducing carbonyl-containing compounds. Because of the special mode of fusion of the quinolizidine residues, a larger number of stereoisomers can be expected in the matrine than in the sparteine series. Four stereoisomers—matridine (LXIIa), allomatridine (LXIIb), isosophoridane (LXIIc), and sophoridane (LXIId)—have been obtained from the corresponding naturally occurring or synthetic compounds of the matrine series containing a carbonyl group in the *D* ring.

(LXIIa)

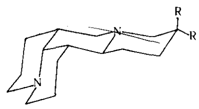

(LXIIb)


(LXIIc)

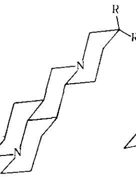


(LXIId)

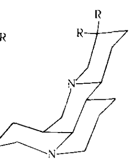
The main peaks in the mass spectra of these compounds[25] are due to c + 1, e, e − 1, g, o, and p ions. From their structures it could be supposed that these ions would be formed most efficiently by the rupture of bonds in the *C* ring. The ions p and o (*m/e* 137 and 136) would then contain the *A* + *B* ring system, the c + 1 ion (84) the *D* ring, and the e, e − 1, and g ions (97, 96, and 98) the *D* ring and the $C_{(17)}$ atom. However, incomplete data for the mass spectrum of the 15,15-dideutero-analogue of matridine[26] indicate that the *D* ring is almost completely absent from g ions, which are therefore formed by the rupture of at least three bonds in rings *A* (or *B*) and *C*. This result seemed to the Reviewers unexpected and requiring further refinement. A mass-spectrometric investigation was therefore undertaken on the 14,14-dideutero-analogues both of matridine itself (LXIIa) and of its stereoisomers (LXIIb, *c*).[25] This revealed the clear influence of the stereochemistry of these compounds on their mode of breakdown under electron bombardment.



(LXIIa) R = H
14,14-D2-matridine, R = D



(LXIIb) R = H
14,14-D2-allomatridine, R = D



(LXIIc) R = H
14,14-D2-isosophoridane, R = D

The mass spectra of the unlabelled compounds (LXIIa–*d*) are qualitatively similar, but quantitatively allomatridine (LXIIb) resembles sophoridane (LXIId), while matridine (LXIIa) resembles isosophoridane (LXIIc). The most noticeable feature of the spectra of the first two stereoisomers is predominance of peaks due to the molecular ions, whereas the peaks of the p ion (*m/e* 137) are dominant in the spectra of the second pair. The great stability of molecular ions of (LXIIb) and (LXIId) may obviously be due to the predominantly *trans*-fusion of rings in their tetracyclic system: in the former all the rings are *trans*-fused, and in the latter *A*–*B*, *A*–*C*, and *B*–*C trans*-fusion can be regarded as proved, while the type of fusion of rings *C* and *D* has not been finally proved[27,28]. Matridine (LXIIa) and isosophoridane (XLIIc), however, each contain two energetically less favourable *cis*-fused systems.

There are also other quantitative differences in the mass spectra of these stereoisomers, which cannot yet be explained owing to the absence of additional data on the elementary composition of the ions, the mechanisms of their formation, and the energetics of the molecules.

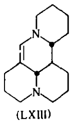
Comparison of the mass spectra of the 14,14-dideutero-analogues of matridine, allomatridine, and isosophoridane with those of the unlabelled alkaloids showed[25] that such characteristic peaks as those due to ions having *m/e* 151, 150 (y + 1), 137 (p), 136 (o), and 96 (e − 1) are not displaced by the introduction of the deuterium label at position 14: i.e. with these compounds the ions result from localisation of charge on the 1-nitrogen atom and do not contain the *D* ring. Yet the peaks of ions with *m/e* 98 and 84 (g and c + 1) differ in structure depending on the stereochemistry of the compound.

The peaks of g ions from matridine and isosophoridane are only ~24% and ~27% respectively due to ions containing the *D* ring, the majority of these ions resulting from localisation of charge on the 1-nitrogen atom and containing an *A* or *B* ring. Consequently, different mechanisms of formation of g ions can be assumed for these compounds, each involving the rupture of at least three carbon–carbon bonds. In the absence of the spectra of deuterated analogues labelled in either ring *A*, *B*, or *C*, however, it is difficult to make any definite statement. In the decomposition of allomatridine, in contrast to the above two compounds, the g ion is formed predominantly (~80%) by charge localisation on the 16-nitrogen atom and contains the *D* ring. In this case the mechanism of formation evidently involves cleavage of the $C_{(7)}$–$C_{(11)}$ and $C_{(5)}$–$C_{(17)}$ bonds with migration of a hydrogen atom to the charged particle.

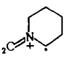
The above differences in the breakdown paths of the stereoisomers of matridine can obviously be attributed to the fact that in (LXIIb) all ring fusions are *trans*, whereas in (LXIIa) the *A*–*C* and *B*–*C* fusions are *cis*, as are the *A*–*B* and *A*–*C* fusions in (LXIIc). A primary consequence may be the facilitation of bond fission in the *A*, *B*, and *C* rings of molecular ions of the latter two compounds, whereas in the first compound the bonds are equally strong in all rings, so that here the most advantageous process occurs, involving the rupture of two bonds in the *C* ring. It must also be borne in mind that the g ion can undergo rearrangement, so that its ease of formation may be influenced not only by the energy factor but also by the distance between the centres of migration.

The stereochemistry of the tetracyclic skeleton of compounds (LXIIa–*d*) influences also the decomposition routes leading to formation of the rearranging c + 1 ions. The mass spectra of the 14,14-dideuterated analogues of allomatridine and isosophoridane contain corresponding peaks displaced by 2 amu and to some extent by 1 amu: i.e. with these compounds the c + 1 ion contains predominantly the *D* ring. In the spectrum of 14,14-dideutero-matridine, however, the 1-amu displacement of the peak of this ion is only slight.

It is noteworthy that the c + 1, e, e − 1, and g ions are almost completely absent from the spectrum of 5,17-dehydroallomatridine (LXIII),[20] but an intense peak of an ion having *m/e* 95 appears.



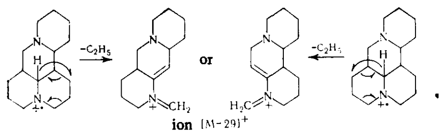
(LXIII)



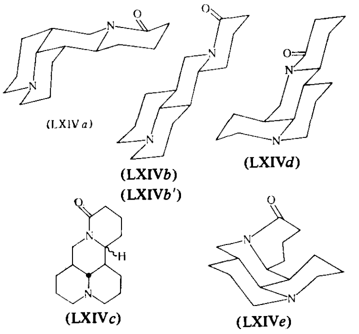
m/e 95

The mass spectra of (LXIIa) and (LXIIc) contain fairly intense ion peaks at 162, which are only small in the case of stereoisomers of sparteine. However, an ion with *m/e* 162 can hardly be diagnostically significant, since the intensity of its peak is also small in the spectrum of (LXII*b*). It is difficult to judge the origin of this ion; we know only that it contains neither the $C_{(14)}$ [26] nor the $C_{(15)}$ [25] atom, and has the composition $C_{11}H_{16}N$ according to the high-resolution mass spectrum of (LXII*c*).[21]

The spectra of (LXII*a–d*) contain also weak peaks of $[M - 43]^+$ and $[M - 29]^+$ ions but, in contrast to those of sparteine stereoisomers, no $[M - 41]$ peaks. It is supposed[21,29] that the $[M - 43]^+$ ion is formed by elimination of a propyl radical or an aziridine molecule. Formation of the $[M - 29]^+$ ion, however, is regarded as involving elimination of an ethyl radical from the *A* or *B* ring, but not from *D*, which is supported by the mass spectra of the 14,14-dideutero-analogues of the stereoisomers (LXII*a–c*) [25]:



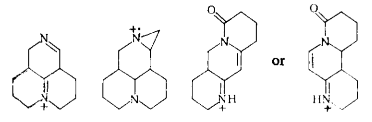
Derivatives of (LXII*a–d*) containing a lactam carbonyl in the *D* ring are often encountered in Nature. Most thorough studies have been made of the mass spectra of matrine (LXIV*a*) [20,21,30], leontine (LXIV*b*) [31], sophoridine (LXIV*c*), the synthetic enantiomer of leontine—allomatrine (LXIV*b′*) and isosophoridine (LXIV*d*).[20,21,30]. Data have appeared[32] on the mass spectrum of darvasamine (LXIV*e*), which was regarded as the first naturally occurring *cis*-*A*–*B* stereoisomer of matrine.


(LXIV*a*)
(LXIV*b*)
(LXIV*b′*)
(LXIV*d*)
(LXIV*c*)
(LXIV*e*)

The most characteristic feature of the mass spectra of these compounds in comparison with those of their isomers in the sparteine series (lupanine and *α*-isolupanine) comprises the exceptionally intense peaks of molecular and $[M - 1]^+$ ions, the former being rather higher in the case of matrine (LXIV*a*), with the opposite relation in the spectra of the other stereoisomers. Formation of the $[M - 1]^+$ ion is assumed to involve elimination of the 6-hydrogen atom. This may well be so, since the majority of $[M - 1]^+$ ions from quinolizidine itself (I) are formed by ejection of the hydrogen atom from the angular position 10 (Section II).[5] An attempt to relate the stability of the polycyclic system solely with the intensity of the molecular ion peaks was unsuccessful, since all these compounds (LXIV*a–d*) exhibited similar intensities of these ions measured as percentages of the total ion current[31]. Nevertheless, the sum of the intensities of molecular and $[M - 1]^+$ ion peaks was greatest with leontine (LXIV*b*), in agreement with the least stress in the completely *trans*-fused tetracyclic system. Matrine exhibits the lowest sum of the peak intensities of these ions.

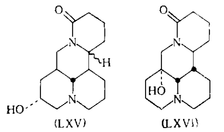
Among ions representing the quinolizidine system formed by rings *A* and *B* in the molecules (LXIV*a–d*) the peaks due to **c**, **c** + 1, **e**, and **g** are lower in their spectra than in those of oxygen-free derivatives in the cytisine, sparteine, and matridine series. In the case of compounds (LXIV*a–d*) these ions in fact result exclusively from rings *A* and *B*, which is confirmed by the unchanged position of their peaks when a deuterium label is introduced into the *D* ring.[20,21] The peaks of o and p ions are moderately intense. The presence of the corresponding metastable peak in the spectrum of matrine indicates that in this case the o ion may be formed directly from the molecular ion[20,21].

In contrast to the corresponding isomers in the sparteine series, spectra of the stereoisomers (LXIV*a–d*) contain, in the range from *m/e* 150 to the molecular ion, fairly intense peaks due mainly to cleavage of bonds in the *D* ring. The high-resolution mass spectrum of (LXIV*a*) indicated[20,21] that the ion with *m/e* 161 had the composition $C_{10}H_{11}NO$, whereas the 162 ion was due to $C_{10}H_{12}NO$ and $C_{11}H_{16}N$ ions in the proportion 55 : 45. An appreciable peak at 177, most characteristic in the spectrum of allomatrine, was due to the $C_{11}H_{17}N_2$ ion formed by elimination of the *D* ring. Elimination of part of the latter from (LXIV*a–d*) as C_3H_4O gave a comparatively stable $C_{12}H_{20}N_2$ radical-ion with *m/e* 192.[20,21,26]



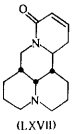
m/e 177
m/e 192
m/e 205

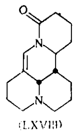
It was shown by deuterium labelling[20,21] that a propyl radical could be eliminated from ring *A* or *B*, to give an ion with *m/e* 205. It is interesting that, in contrast to oxygen-free derivatives of the sparteine and matridine series, the $[M - 29]^+$ ion peak of (LXIV*a–d*) is due to $C_{13}H_{19}N_2O$ and $C_{14}H_{23}N_3$ ions[20,21], which have therefore been formed by elimination of an ethyl radical and of (CO + H) respectively.


(LXV)
(LXVI)

The structure of the alkaloid 3*α*-hydroxysophoridine (LXV) was established from the rules of the breakdown of molecular ions of matrine and sophoridine[13]. The presence of the hydroxy-group in (LXV) and also in sophoranol (5*α*-hydroxymatrine) (LXVI) [20,21] is the reason for the appearance of $[M - 17]^+$ ion peaks in their mass spectra, these being the highest in that of (LXVI). The majority of peaks in this spectrum arise directly from the molecular ion, so that peaks typical of matrine (LXIV*a*) are displaced by 16 amu to larger masses, since most of these ions include *A* and *B* rings. For example, the e − 1 peak (*m/e* 96) is accompanied in the spectrum of (LXVI) by an ion peak at 112. The origin of these peaks was confirmed by analysing the mass spectrum of 6,7-dideuterosophoranol.[20,21]

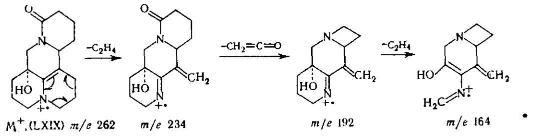
Breakdown of the molecular ion of sophocarpine—13,14-dehydromatrine (LXVII) [26,30]—follows the same routes as that of matrine. Ions containing the *A–C* ring system have the same mass numbers in the two cases, whereas ions resulting from cleavage of ring *A* or *B* are 2 amu lighter from the former compound. This applies e.g. to the $[M-29]^+$ and $[M-43]^+$ ions, produced by elimination of an ethyl or a propyl radical from ring *A* or *B*.


(LXVII)

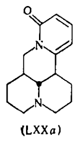

(LXVIII)

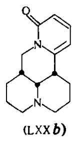
The presence of a double bond in ring *C*, as in leontalbine—5,17-dehydromatrine (LXVIII)—inhibits processes involving cleavage of this ring[26]. At the same time ring *D* may be eliminated either entirely with formation of an ion having *m/e* 175 (a dehydro-analogue of the 177 ion in the case of matrine) or partly to give the $[M - C_3H_4O]^+$ ion. The $[M-29]^+$ and $[M-43]^+$ ion peaks in the spectrum of matrine have been replaced in that of leontalbine (LXVIII) by peaks due to $[M-28]^+$ and $[M-42]^+$ ions.

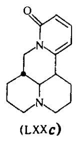
In contrast to sophoranol (LXVI), the intensity of the $[M-17]^+$ peak drops sharply in the spectrum of 6,7-dehydro-5-hydroxymatrine (LXIX) [20,21], and the molecular-ion peak is accompanied by an equal peak of the $[M-1]^+$ ion. The $[M-28]$ peak (*m/e* 234) is much more intense in the spectrum of (LXIX), but weak in all the above spectra of matrine alkaloids. Its considerable intensity is most likely due to the possibility of a retrodiene type of decomposition in ring *B*:

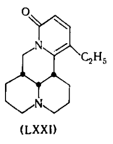


Further decomposition of the 234 ion involves either elimination of a hydroxyl radical to form a 217 ion, whose peak is among the most intense in the spectrum, or elimination of a keten molecule to give a 192 ion, which then undergoes a retrodiene breakdown with elimination of an ethylene molecule and formation of an ion with *m/e* 164. A keten molecule is eliminated also from the 217 ion, to give a 175 ion.


(LXX*a*)


(LXX*b*)


(LXX*c*)

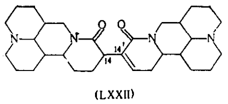


(LXXI)

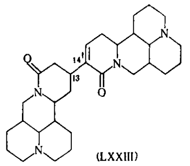
Aromatisation of the *D* ring in matrine alkaloids increases still further the difference between their mass spectra and those of the corresponding derivatives in the sparteine series (see above). As with the stereoisomers of matrine, peaks due to molecular and $[M-1]^+$ ions exhibit great (sometimes maximum) intensity in the spectra of isosophoramine (LXX*a*) [20,21,30], sophoramine (LXX*b*) [20,30], neosophoramine (LXX*c*) [33], and 12-ethylsophoramine (LXXI) [20], whereas peaks due to g ions (*m/e* 98) containing the *D* ring dominate the spectra of the corresponding sparteine derivatives (above). It is interesting that the change in the relative intensities of molecular and $[M-1]^+$ ion peaks on passing from isosophoramine (LXX*a*) to sophoramine (LXX*b*) is analogous to the change on passing from allomatrine to matrine (above). This is obviously connected with the analogy in the stereochemistry of the fusion of rings *A*, *B*, and *C* in these two pairs of compounds. The intensities of peaks due to g ions are very weak in the spectra of (LXX*a*–*c*) and (LXXI), since their formation from ring *A* or *B* requires the rupture of more than two bonds, which is obviously disadvantageous. One of the most intense peaks in the spectra of (LXX*b*), (LXX*c*)†, and (LXXI) is that of the o ion (*m/e* 136), while the peaks at 146 and 160 (v and q) typical of the spectra of anagyrine and *d*-thermopsine (above), are small and shift by 28 amu to *m/e* 174 and 188 on passing to (LXXI).

The stereochemistry of the molecules (LXX*a*–*c*) has a fairly significant quantitative influence on their spectra. Thus (LXX*a*) is characterised by high intensity of the y ion peak (*m/e* 149), while that of the o peak drops sharply. The opposite pattern is found for the spectra of (LXX*b*) and (LXX*c*), however, and with the latter compound all peaks are weak other than those of molecular, $[M-1]^+$, and o ions. According to the high-resolution mass spectrum of (LXX*a*) the not very intense peaks (around 15–25% of the maximum) of $[M-29]^+$ ions with *m/e* 215, present in the spectra of all three isomers, represent the compositions $C_{13}H_{15}N_2O$ and $C_{14}H_{19}N_2$. Hence they are formed by elimination either of an ethyl radical or of a carbonyl group together with a hydrogen atom[20,21].

The mass spectra of goebeline—the naturally occurring dimeric matrine alkaloid—and its dihydro-derivative have been given[34] to establish their structure, but with no unambiguous evidence for the suggested site (14,14′) of linking of the two moieties (LXXII). We can accept that the goebeline molecule comprises residues of matrine and sophocarpine or their stereoisomers. The mass spectrum of goebeline contains a peak due to the molecular ion together with a pair of peaks corresponding to the molecular and $[M-1]^+$ ions of sophocarpine, though the remainder of the spectrum below this pair differs quite strongly from the spectrum of sophocarpine with respect to the intensities of the peaks.

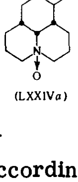


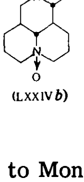
(LXXII)

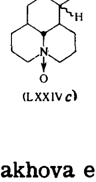


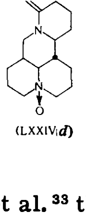
(LXXIII)

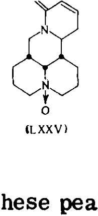
The mass spectrum of deuterated goebeline, obtained by exchange with deuteroethanol in the presence of sodium deuteroxide in oxolan, indicates the predominant incorporation of four deuterium atoms[20]. This excludes the possibility of 14,14′-linking of matrine and sophocarpine residues, since the same method of deuteration introduces two and three deuterium atoms into the former and into the latter respectively, whereas only three deuterium atoms should enter with 14,14′-linking. The Reviewers regard 13,14′-linking of matrine and sophocarpine residues (LXXIII) as most probable, although this question is by no means finally settled.

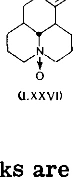

(LXXIV*a*)


(LXXIV*b*)


(LXXIV*c*)


(LXXIV*d*)


(LXXV)


(LXXVI)

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† According to Monakhova et al.[33] these peaks are maxima in the spectra of (LXX*b*) and (LXX*c*), which for the former compound is inconsistent with other results[20].

In conclusion we must consider briefly a mass-spectrometric study of *N*-oxides of matrine (LXXIV*a*), allomatrine (LXXIV*b*), sophoridine (LXXIV*c*), isosophoridine (LXXIV*d*), sophocarpine (LXXV), and isosophoramine (LXXVI).[35] Their mass spectra usually contain weak peaks of the molecular ions. The $[M-16]^+$ and $[M-17]^+$ peaks are considerably more intense, and sometimes the main peaks in the spectra. The first peak in this pair is due to elimination of an oxygen atom, whereas the second peak may be due to various processes—further loss of a hydrogen atom from the $[M-16]$ ion, single-stage ejection of the *N*-oxide oxygen and a hydroxyl hydrogen atom, or elimination of an oxygen atom from the $[M-1]^+$ ion. Comparison of the ratios $I[M-17]^+/I[M-16]^+$ in the spectra of the *N*-oxides and $I[M-1]^+/I[M]^+$ in those of the corresponding unoxidised alkaloids indicates that the first of these paths is insignificant. Yet the presence of the corresponding metastable peaks in the spectra of the *N*-oxides is evidence that $[M-17]^+$ ions are formed at least partly by elimination of a hydroxyl radical from the molecular ions in a single stage. The hydrogen atom present in this radical has been eliminated from a different position from that from which the hydrogen atom is eliminated from the unoxidised alkaloids to form the $[M-1]^+$ ions.

The majority of ions produced by electron bombardment of the *N*-oxides are formed directly from $[M-17]^+$ ion. The mass spectra of the stereoisomeric *N*-oxides [LXXIV*a*–*d*) differ quantitatively among themselves mainly in the relative intensities of the $[M-16]^+$, $[M-17]^+$, $[M-18]^+$, and $[M-19]^+$ ion peaks, as well as of the peaks having m/e 148 and 150. In general the spectra of the *N*-oxides in the range of mass numbers below the $[M-17]$ peaks resemble those of the corresponding unoxidised alkaloids, but the peaks of ions characteristic of the latter are often accompanied by peaks 1 amu lower, which proves that they are due to ions containing rings *A* and *B*.

Thus all the results surveyed above provide convincing evidence that mass spectrometry can be used to assign quinolizidine alkaloids to a particular series, to determine the nature and the position of functional groups, to establish the structure of new alkaloids of this class, and in some cases also to elucidate the stereochemistry of ring fusion.

While the manuscript was being prepared for the press a more detailed study appeared[36] of the fragmentation of deoxynupharidine (XVI) and related alkaloids involving the use of high-resolution mass spectra and deuterated analogues.

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Problems in Investigation of the Aroma of Foodstuffs and the Production of Imitations

R.V.Golovnya

General principles of the investigation of volatile components of foodstuffs are discussed, as well as the state of the problem of flavoured food additives. Aspects of the conferment of taste and odour on new types of food are considered. A list of 82 references is included.

CONTENTS

I. INTRODUCTION

In the majority of developed countries industrial methods for the production of food products are continually being intensified. The consequent acceleration of technical processes for the manufacture of various types of nutritional products frequently results in loss of flavour. The insufficiency of full-value protein in feeding the population (the annual world protein deficit exceeds three million tonnes[1]) has made it necessary to obtain by industrial methods new types of food based on protein concentrates, and both taste and odour must be entirely created for these products.

II. DEVELOPMENT OF THE PRODUCTION OF FOOD ADDITIVES AND FLAVOURINGS

Table 1 demonstrates the consumption of protein concentrates in the manufacture of various food products in the USA based on statistics for 1972.[2] During 1969 protein concentrates were added in almost all categories of products, especially in the manufacture of conserved meats and intermediate products. It is predicted that by 1980 a new artificial product—a milk substitute—will have appeared, and it is planned to consume another 188 million lb of protein concentrates for this purpose. A total of about a million tons of protein additives will be used in the USA foodstuffs industry in 1980. According to forecasts made in 1971 by a long-term planning service, the 1985 production of meat and poultry substitutes and of milk products in Western Europe will be respectively 2.8 and ~3.5 million tonnes[3].

Loss of flavour in food manufacture and the necessity of obtaining products from protein concentrates are the chief reasons for the sharp increase in the demand for flavourings and flavour and odour intensifiers. Demand doubled during the decade from 1955 to 1966, and continues to grow. Even the term "flavour renaissance" has now appeared (the complex of tactile, gustatory, and olfactory sensations caused by foods is denoted by the word *flavour*).

Aromatising and flavouring additives constitute 15–20% of the total cost of a foodstuff from a protein concentrate[2,4]. A vivid example of the economic advantage of the development of scientific and applied research, as well as the production of flavourings and taste and odour intensifiers, is provided by returns (Table 2) for 1971 and the forecasts for 1980 made by the American firm Frost and Sullivan Inc.[4]

Table 1. Growth of consumption of protein concentrates in the manufacture of various foodstuffs in the USA.

Product category	Planned annual increase, %	Protein additions, 10^6 lb	
		1969	1980
Baby foods	1.0	3.5	3.9
Bread and bakery products	7.5	101.0	126.1
Convenience meals	9.7	17.9	36.0
Confectionery	3.0	16.6	23.0
Cooked meats and semimanufactures	19.3	92.2	642.4
Coffee whiteners	6.0	12.0	22.8
Milk substitutes	—	—	188.2
Synthetic ice cream	5.0	3.8	6.5
Other types of milk products	1.0	98.1	109.1
Desserts	6.0	31.7	60.0
Dietetic products	2.0	8.7	105.0
Frozen foods	3.6	3.8	5.6
Macaroni and pasta products	3.0	1.5	2.1
Animal fodder	5.4	229.3	426.0
Soups	0.0	1.5	1.5
Other uses	9.3	207.3	555.0
Total quantity		828.6	$2218.5 \simeq 10^6$ tons

Table 2. Income from use of food additives (millions of dollars).

Year	Food additives	
	total	flavourings and taste intensifiers
1971	635.97	254.00
1975	804.19	326.90
1980	1108.81	476.40

Since 1958 the Flavoring Extract Manufacturers Association (FEMA) has conducted a programme aimed at establishing a statute on flavourings. All known natural and synthetic compounds employed in the food industry up to 1958 have been tested for toxicity, pharmacological effect, and metabolism in the organism both of the substance itself and of its derivatives, in six academic institutions independent of industry. A list of GRAS substances ("generally recognised as safe") has been published systematically; it includes 1121 natural and synthetic compounds, with the permissible dosage for each category of foodstuffs (drinks, ice cream, confectionery, bread and bakery products, jellies, puddings, meat, sauces, soups, milk products, pickles, seasonings, etc.)[5,6]. The number of compounds used in the food industry before 1958 that failed the test was 267, including some natural substances[7]. Of the 1121 GRAS substances 859 are used in the food industry (at a maximum dosage of 10 ppm—by volume or by weight) to flavour the foodstuff. The list of GRAS substances is extended systematically and published annually.

The modern flavourings industry is based on substances detected in the odour of natural foodstuffs, in contrast to the earlier period, when restrictions were imposed by similarity of odour and inferred toxicity. The new approach has led in several cases to qualitatively new types of imitations, indistinguishable from the natural products, since they include the key substances responsible for the odour of the latter. For example, ethyl *αβ*-epoxy-*α*-methyl-*β*-phenylpropionate has the odour of strawberries[8], 4-*p*-hydroxyphenylbutan-2-one that of raspberries[9,10], allyl phenoxyacetate pineapple[11], 2-isobutyl-3-methoxypyrazine pepper[12-14], and diallyl trisulphide garlic[15]; this last compound also possesses bactericidal properties.

III. ISOLATION AND ANALYSIS OF ODOUR COMPONENTS

Substantial difficulties arise in the investigation of the odour of natural foodstuffs. Man is able to distinguish up to 17 000 odours[16]. Since a theory of olfaction is lacking, aroma cannot be predicted from the physical and chemical properties of the molecule. The minuteness of the content of odour condensate in a specimen is responsible for the difficulties in investigating flavour. But according to Weurman the amounts of odour condensate associated with 1 kg of meat, strawberries, and bread are respectively 35, 2–8, and 8–10 mg.[17,18] The number of different substances in an odour condensate is immense—several hundreds of components belonging to various classes of organic compounds—which in practice always include acids, alcohols, esters, sulphur-containing compounds, amines, ketones, aldehydes, lactones, phenols, hydrocarbons, etc. with a wide range of boiling points, from gases to compounds boiling at 300°C.

The substances determining the character of the odour often have low threshold concentrations—of the order of 10^{-12}–10^{-14} part per unit volume or weight—undetectable by present-day analytical apparatus. The odour threshold for 2-isobutyl-3-methoxypyrazine is 10^{-12}.[14] Clearly, therefore, it is necessary to concentrate the odour in order to study it[19-21].

It must be emphasised also that analytical instruments are like a biological detector—man's olfactory organ—in being unable to estimate the quantity of odour in a complex. Moreover, there is no correlation between the sensory sensitivity of man to individual components and the sensitivity of an analytical instrument. For example, the gas chromatograph is more sensitive to acetone, whereas to vanillin the nose is more sensitive than this instrument by several powers of ten[22] (Table 3).

Table 3. Comparison between the sensitivity of the human nose and that of a chromatograph with a flame-ionisation detector[22].

Compound (in aq. soln.)*	B.p., [°C]	Limit of detection, ppm	
		chromatograph	nose
Propanal	61	0.0025	0.17
Butanal	75.7	0.12	0.07
Hexanal	131	0.3	0.03
Acetone	56	0.3	500
Methanethiol	7.6	0.013	0.002
Methyl salicylate	222	**	$0.1 \cdot 10$
Vanillin	285	**	$0.1 \cdot 10^{-9}$

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* Analysis made on 10 ml of saturated vapour above the solution.

** Undetectable.

The investigation of odour involves mostly study of the composition of volatile components in the vapours above a foodstuff, actually in condensates of these vapours. In the scientific literature the special term "head-space analysis" has become attached to such an approach[23]. The quantity of a substance in the vapour above a food is not equivalent to its actual content in the latter. The vapour pressure P_{ia} of a substance i in the gas phase over a foodstuff is given by the formula[23]

$$P_{ia} = \gamma_i X_i P_i, \qquad (1)$$

where P_i is the saturated vapour pressure of pure i at the same temperature, X_i the mole fraction of i in the foodstuff, and γ_i its activity coefficient at this concentration.

At a constant mole fraction X_i the value of γ_i may vary by several powers of ten depending on the nature of the substance and of the medium in which it is situated[24]. In the aqueous phase of a foodstuff, for example, the activity coefficient may depend on the concentration of metal salts, their capacity for complex formation with the test substance, and also the pH. The proportions of components in the vapour over a product varies with the content of water, lipids, proteins, and other ingredients of the sample. Furthermore, several substances are present in a foodstuff in a combined state, as "precursors" from which they pass into the gas phase as a result of enzymatic or chemical reactions. Therefore samples of the same foodstuff prepared at different times from different batches of raw material may exhibit both qualitative and quantitative differences in the volatile components of the odour concentrate.

Equation (1) is valid under equilibrium conditions. On prolonged collection of volatile components the rate of diffusion from the specimen to the gas phase changes, which may distort the proportions of volatiles in the condensate in comparison with the gas phase above the specimen. For this reason volatiles are collected above the specimen only as long as the latter retains its full flavour, and the condensate has the same odour.

The influence of the above factors on the process of concentrating the aromatic components makes it almost impossible to obtain quantitative data on the total composition of odour components in a test product. However, analysis of the odour condensate enables the substances involved in forming the flavour to be studied, and their proportions in the composition to be determined. Gas-chromatographic and organoleptic investigations enable "key" components of the odour to be detected and identified. More than 2500 compounds have now been identified in the odour of various foodstuffs[25], the number increasing every year.

Separation and *identification* are necessary stages in the investigation of an odour concentrate. Gas–liquid chromatography is the only method suitable for the separation of multicomponent mixtures of volatiles of unknown composition. The detection of individual compounds and their identification can be accomplished gas-chromatographically, mass-spectrometrically, and by infrared and nuclear magnetic resonance spectroscopy. The last two methods are generally employed when components can be isolated and accumulated by preparative chromatography. Difficulties are aggravated by the fact that the majority of flavour-forming substances studied have odour thresholds in the range 10–100 pg.[23] Hence there is hardly a single present-day analytical method that can ensure reliable determination of all the organic compounds in the volatile components of natural mixtures. The absence of direct methods of analysis of the required sensitivity makes the stages of extraction and concentration of the odour components especially important. A critical approach is required to the choice of method for these stages, for treating the odour concentrate right until the specimen to be analysed is introduced into the chromatograph. Every stage requires maximum protection of the mixture from contamination and possible loss of components, with especially careful purification of solvents. Sources of error in obtaining a sample for analysis have been discussed[26]. It must also be borne in mind that if the whole of the odour concentrate undergoes gas-chromatographic analysis, it is difficult to exclude artefacts and the formation of new substances by the interaction of reactive compounds directly in the gas-chromatographic column, or even in the vaporiser under the influence of the temperature, the material of the column, and its adsorbent.

Inspection of published information has shown that special gas-chromatographic methods of identification are required for the examination of complicated natural flavouring mixtures. It is impossible to prepare a gas-chromatographic column capable of separating simultaneously diverse classes of organic compounds. Furthermore, identification by means of standard substances, in the study of mixtures containing up to 400 or more components, presents considerable difficulties, even with the use of mass-spectrometric detection.

An odour concentrate can be investigated in two ways: it can be either chromatographed as a whole or first divided into different classes of organic compounds, which are chromatographed separately. In order to diminish the artefacts and to utilise most fully the specific donor–acceptor interactions between the test substance and the adsorbent in the gas-chromatographic column it is more advisable to separate complicated odour compositions into individual classes of organic compounds having the same type of functional groups. Methods of gas-chromatrographic identification using a set of columns of differing polarity are found for each class of organic compounds[27–43].

In the separation and analysis of multicomponent mixtures the reproducibility of the gas-chromatographic results over a long period of time, which is necessary in the study of different specimens of a test material, becomes especially important. Experience of analysing the odour of natural foodstuffs has permitted comparison of the reproducibility of different gas-chromatographic characteristics[27]. The most convenient and reproducible gas-chromatographic parameter—the Kovats index—has been selected and recommended, and a theoretical justification provided for the use of an ideal series of n-alkanes in its calculation[27]. In the analysis of multicomponent mixtures it is almost impossible to place every test substance between two n-alkanes, as the Kovats formula requires[44]. I therefore propose to calculate the indices on the basis of an "ideal" series of n-alkanes constructed from three or four experimental values of the logarithms of corrected retention volumes of n-alkanes containing $n \geqslant 6$ carbon atoms, i.e. to find the coefficients in the linear equation

$$\lg V'_n = a + bn. \tag{2}$$

The legitimacy of employing an "ideal" series of straight-chain hydrocarbons for the calculation of Kovats indices was examined separately on the basis of experimental data in McReynolds' tables[45] on the retention of n-alkanes by 13 stationary phases. The accuracy of Eqn. (2) and of known non-linear equations[46,47] describing the gas-chromatographic behaviour of n-alkanes was estimated statistically on an electronic computer. It was shown that the linear approximation (2) provided quite satisfactory accuracy (0.8%) abd could be used in gas-liquid chromatography for identification purposes and for the calculation of thermodynamic functions from retention indices. Use of an "ideal" series of n-alkanes simplifies the calculation and makes the system of retention indices extremely convenient for the study of natural mixtures. It was shown also that the time required for analysis could be shortened by the use of an arithmetic retention index, which was converted by means of the "ideal" series of n-alkanes into the Kovats index[48] in order to obtain more information on the structure of the compound.

Natural mixtures can be investigated by gas chromatography either under isothermal conditions or with temperature programming. The most accurate gas-chromatographic parameters required for identification can be obtained by isothermal analysis. With linear temperature programming the only reliable retention parameter is the index I_{lin} calculated by means of the formula in Ref. 49. In order to obtain information on the structure of a compound, the dependence of this index on the experimental conditions was examined, and a correlation was found with the isometric index. A formula was deduced theoretically for the equivalent isothermal index $I_{T_0/\beta}$, so that it became possible to identify the components of an odour from an analysis with a programmed column temperature[36]. The formula enables $I_{T_0/\beta}$ to be calculated in terms of parameters characterising the experimental conditions:

$$I_{T_0/\beta} = I_{T_0} + \frac{\beta\tau_x}{2}\cdot\frac{\partial I}{\partial T},$$

where I_{T_0} is the isothermal index with T_0 the initial temperature of the analysis, β (deg min^{-1}) the rate of the programmed variation of temperature, τ_x (min) the retention time of the substance in the column, and $\partial I/\partial T$ the temperature gradient of the index.

Retention indices are convenient in being directly related to the free energy of sorption of the test substance during chromatography. Equations have been found which enable experimental indices to be used for a quantitative estimate of the gas-chromatographic sorption process based on thermodynamic functions—partial molar enthalpies, entropies, and free energies of dissolution, as well as the differences in the corresponding excess thermodynamic functions of mixing ΔH^E, ΔS^E, and ΔG^E.[50-54] The proposed set of equations, relating the indices with the thermodynamic functions of sorption, enabled optimum conditions to be selected for gas-chromatographic separation and methods of identification to be developed without the use of standard substances[27].

IV. METHODS OF IDENTIFICATION WITHOUT THE USE OF STANDARD SUBSTANCES

The name "identification without standards" is applied to a method involving the special selection, for a mixture of substances having the same type of functional groups, of a set of columns of ensure optimum conditions of separation and to permit mathematical expression of the dependence of the gas-chromatographic behaviour of a substance on its physicochemical properties. The chosen system of columns enables relative retention parameters to be used for identification, without the help of standard substances. Scheme 1 lists the set of columns recommended for the identification of various classes of organic compounds. Each system is selected to diminish the probability of errors due to the overlapping of chromatographic zones in the column.

Scheme 1

Amines

$T = 100°C$	$T = 100°C$
10% tristearin	4% Apiezon-L + 1% Na_3PO_4
5% mineral oil + 2% KOH	5% Triton X-305 + 0.5% Na_3PO_4
10% Tween-80	5% PEG-1000 + 0.5% Na_3PO_4
10% PEG-1000	3% tetrakishydroxyethylaziridine + 2% PEG-1000 + 0.5% Na_3PO_4
on Novator detergent at pH 11.5	on Chromosorb G

Monocarbonyl organic compounds

$T = 50, 125°C$	Programmed temp.
10% Apiezon-M	10% Apiezon-M
10% PEGA	10% PEGA
10% oxy-$\beta\beta'$-dipropionitrile	

Sulphur-containing compounds

$T = 60, 130°C$

10% Apiezon-M
10% Triton X-305
10% silicone OV-17
10% PEG-1000
on Chromosorb W

The set of four columns of differing polarity listed on the left of Scheme 1 was originally proposed for analysing a mixture of aliphatic amines and heterocyclic bases. The support used was Novator detergent. The donor-acceptor interaction observed between amines and phosphates[55,56] permitted the development of a practically new method for the analysis of amines[34]. The alkali was replaced by trisodium phosphate, and the detergent by Chromosorb G. The set of four columns listed on the right of Scheme 1 was proposed for the identification of amines among the components of an odour. Organic monocarbonyl compounds among the volatile components of natural materials were to be identified by the set of columns on the left (also the list on the right for analysis under isometric conditions) with temperature progamming[35-38]. A system of four stationary phases on Chromosorb W (see Scheme 1) has also been selected for the analysis of complicated mixtures containing thiols, sulphides, disulphides, and sulphur heterocycles together; this method enables substances having boiling points up to 280°C to be identified[41-43].

Table 4. Equations correlating retention indices I^* with the number of carbon atoms n in a straight-chain aliphatic amine for analysis at 100°C (Na_3PO_4)**, where m the ordinal number of the homologue.

Primary amines		Secondary amines		Tertiary amines
$I^{Ap}=100n+234+45/n$	$m\geqslant1$	$I^{Ap}=100n+134+104/n$	$m\geqslant2$	$I^{Ap}=85n+149;\ m\geqslant3$
$I^{Ap}=100n+241$	$m\geqslant3$	$I^{Ap}=100n+146$	$m\geqslant3$	
$I^{Tr}=100n+460-28/n$	$m\geqslant2$	$I^{Tr}=111n+84+744/n$	$m\geqslant2$	$I^{Tr}=86n+177;\ m\geqslant3$
$I^{Tr}=100n+455$	$m\geqslant3$	$I^{Tr}=100n+270$	$m\geqslant3$	
$I^{PEG}=100n+566-36/n$	$m\geqslant2$	$I^{PEG}=100n+319+90/n$	$m\geqslant2$	$I^{PEG}=85n+188;\ m\geqslant3$
$I^{PEG}=102n+547$		$I^{PEG}=100n+330$	$m\geqslant3$	
$I^{TH+PEG}=96n+686+6/n$	$m\geqslant2$	$I^{TH+PEG}=100n+329+46/n$	$m\geqslant2$	$I^{TH+PEG}=86n+200;\ m\geqslant3$
$I^{TH+PEG}=96n+686$		$I^{TH+PEG}=94n+435$	$m\geqslant3$	

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* Stationary phases: Ap = Apiezon-L; Tr = Triton X-305; PEG = polyethylene glycol 1000; TH + PEG = tetrakishydroxyethylaziridine with polyethylene glycol 1000.

** Columns treated with trisodium phosphate as in Ref.34.

Table 5. Equations correlating retention indices I with number of carbon atoms n in carbonyl compounds*.

Temperature of analysis 50°C		
Alkanals	Alkan-2-ones	Alk-2-enals
$I^{Ap\text{-}M}=100n+170$	$I^{Ap\text{-}M}=100n+153$	$I^{Ap\text{-}M}=100n+228$
$I^{DNP}=100n+285$	$I^{DNP}=100n+278$	$I^{DNP}=100n+369$
$I^{PEGA}=100n+497$	$I^{PEGA}=97n+521$	$I^{PEGA}=90n+690$
$I^{TTP}=100n+397$	$I^{TTP}=100n+399$	$I^{TTP}=100n+513$
$I^{\beta\beta'}=87n+806$	$I^{\beta\beta'}=80n+876$	
$I^{\beta\beta'}=815+86{,}6n-13/n\quad n\geqslant2$	$I^{\beta\beta'}=677+99{,}3n+499/n\quad n\geqslant3$	
Temperature of analysis 125°C		
Alkanals	Alkan-2-ones	Alk-2-enals
$I^{Ap\text{-}M}=100n+177$	$I^{Ap\text{-}M}=100n+157$	$I^{Ap\text{-}M}=100n+235$
$I^{DNP^{**}}=100n+295$	$I^{DNP^{**}}=100n+283$	$I^{DNP^{**}}=100n+378$
$I^{PEGA}=100n+555$	$I^{PEGA}=100n+558$	$I^{PEGA}=97n+734$
	$I^{Ap\text{-}M}=148+100n+64/n;\ n\geqslant3$	
	$I^{PEGA}=520+101n+225/n;\ n\geqslant3$	
Symmetrical ketones	Alka-2,4-dienals	
$I_{125}^{Ap\text{-}M}=100n+140$	$I_{125}^{Ap\text{-}M}=100n+297$	
$I_{125}^{DNP}=100n+251$		
$I_{125}^{PEGA}=100n+492$	$I_{125}^{PEGA}=100n+874$	

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*$I^{Ap\text{-}M}$, I^{DNP}, I^{PEGA}, I^{TTP}, and $I^{\beta\beta'}$ are the retention indices on columns of Apiezon-M, dinonyl phthalate, polyethylene glycol adipate, tritolyl phosphate, and oxy-$\beta\beta'$-dipropionitrile respectively.

**Temperature of analysis 100°C.

A study of 50 amines, 52 monocarbonyl compounds, and 42 sulphur-containing organic compounds has shown that the gas-chromatographic behaviour of homologues is described by a set of equations relating retention indices with numbers of carbon atoms. As an example, the equations for aliphatic amines show (Table 4) that dependence of the index I on the number of carbon atoms n in a compound is described by a set of linear and partial linear equations for each homologous series. Equations of the latter type are convenient for purposes of identification by means of an electronic computer, since they permit the coverage of a further 200 scale units of the indices, whereas linear equations are more convenient for visual interpretation of the chromatograms. Analogous equations for determining numbers of carbon atoms from gas-chromatographic data have been obtained for monocarbonyl compounds (saturated and α-unsaturated aldehydes, methyl ketones, alkadienals, and symmetrical ketones—Table 5), and also for sulphur-containing compounds (thiols, sulphides, and disulphides—Table 6).

Table 6. Equations correlating retention indices I with number of carbon atoms n in sulphur-containing compounds* for analysis at 130°C.

n-Alkanethiols	n-Alkyl sulphides	n-Alkyl disulphides
$I^{Ap\text{-}M}=100{,}3n+336-50/n$; $n\geqslant 2$ $I^{OV}=100{,}9n+411-30/n$; $n\geqslant 2$ $I^{Tr}=100{,}0n+526-54/n$; $n\geqslant 3$ $^{PEG}=99{,}8n+590-45/n$; $n\geqslant 3$	$I^{Ap\text{-}M}=98{,}9n+280+90/n$; $n\geqslant 2$ $I^{OV}=99{,}4n+361+116/n$; $n\geqslant 2$ $I^{Tr}=98{,}5n+434+188/n$; $n\geqslant 2$ $I^{PEG}=98{,}7n+481+230/n$; $n\geqslant 2$	$I^{Ap\text{-}M}=93{,}6n+539+74/n$; $n\geqslant 2$ $I^{OV}=96{,}0n+639+120/n$; $n\geqslant 2$ $I^{Tr}=88{,}5n+793+136/n$; $n\geqslant 2$ $I^{PEG}=87{,}3n+873+155/n$; $n\geqslant 2$
	Isoalkanethiols	
	$I_{130}^{Ap}=103{,}3n+256$; $n\geqslant 3$	$I_{130}^{OV}=105{,}7n+316$; $n\geqslant 3$

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* I^{Ap}, I^{OV}, I^{Tr}, and I^{PEG} are the retention indices on columns of Apiezon-M silicone OV-17, Triton X-305, and polyethylene glycol 1000.

Relations have also been found for all the series by means of which boiling points of homologues can be calculated from experimental values of the indices. The identity of boiling points determined from data on all the columns is a criterion of the correctness of an identification. Table 7 gives as example equations [for amines] together with boiling points derived from the indices, and shows good agreement with published boiling points. Similar sets of equations have been obtained for carbonyl compounds (Table 8). The equations set out in Scheme 2 were found (temperature of analysis 130°C) for determining the boiling points of sulphur-containing compounds from their indices on Apiezon M and OV-17 silicone columns. Table 9 lists boiling points for several sulphur-containing compounds calculated from experimental indices by means of the equations for Apiezon M.

Table 7. Equations correlating retention indices I* of n-alkylamines with their boiling points T_b (Na_3PO_4)**.

Equation	Alkylamine	Boiling point claculated from				Published b.p.
		I^{Ap}	I^{Tr}	I^{PEG}	I^{TH+PEG}	
$T_b=\frac{I^{Ap}}{4.0}-81$	propyl	54.5	57.1	54.6	52.5	49—50
$T_b=\frac{I^{Tr}}{4.1}-127$	butyl	79.8	81.5	79.9	78.6	78—79
	pentyl	104.8	105.9	105.3	104.6	104
$T_b=\frac{I^{PEG}}{4.1}-153$	hexyl	128.8	130.3	129.9	129.9	129—130
	heptyl	154.5	154.7	154.6	154.6	155
$T_b=\frac{I^{TH+PEG}}{3{,}8}-203$	octyl	179.1	179.1	179.2	179.4	179.6
$T_b=666-\frac{1.1084\cdot 10^6}{I^{Ap}+1249}$	dimethyl	7.4	6.7	6.5	7.4	7.0
	diethyl	53.3	53.6	51.9	52.8	55.5
$T_b=500-\frac{4.968\cdot 10^5}{I^{Tr}+400}$	dipropyl	111.0	110.1	109.7	107.7	110.5
	dibutyl	161.3	161.4	162.8	163.7	159.0
$T_b=437-\frac{3.293\cdot 10^5}{I^{PEG}+73}$	dipentyl	203.0	202.0	202.0	199.7	202.5

Tertiary amines :

$$T_b=363-\frac{1.7\cdot 10^5}{I^{TH+PEG}-334}$$

$$T_b=876-\frac{2.0183\cdot 10^6}{I^{Ap}+1890}$$

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* Indices determined at 100°C.

** See footnote to Table 4.

Table 8. Equations correlating retention indices I* of monocarbonyl compounds with their boiling points T_b.

Equation	Compound	Boiling points calculated from				Published b.p.
		I^{Ap-M}	I^{DNP}	I^{PEGA}	$I^{\beta\beta'}$	
1	2	3	4	5	6	7
$T_b=539-\frac{7.2\cdot 10^5}{982+I^{Ap-M}}$	propanal	44	45	45	50	49.5
	butanal	75	75	73	75	75.7
$T_b=563-\frac{8.216\cdot 10^5}{1002+I^{DNP}}$	pentanal	105	104	104	104	103.4
	hexanal	129	129	129	130	129
$T_b=531-\frac{6.836\cdot 10^5}{546+I^{PEGA}}$	heptanal	152	152	152	155	155
	octanal	171	171	172	—	168.5
$T_b=2893-\frac{2\ 546\cdot 10^7}{7884+I^{\beta\beta'}}$	nonanal	189	189	190	—	185
	decanal	206	205	206	—	208.5
$T_b=1098-\frac{3.587\cdot 10^6}{2953+I^{Ap-M}}$	propenal	53	53	53	—	52.5
	but-2-enal	98	101	104	—	102.2
$T_b=6380-\frac{1.7144\cdot 10^8}{27\ 230-I^{DNP}}$	pent-2-enal	126	126	125	—	125
	hex-2-enal	151	—	149	—	150
$T_b=-730+\frac{3.019\cdot 10^6}{4746-I^{PEGA}}$	hept-2-enal	176	176	175	—	175
$T_b=674-\frac{1.317\cdot 10^6}{1661+I^{Ap-M}}$	propanone	56	57	56	56	56
	butan-2-one	83	85	81	80	79.6
$T_b=721-\frac{1.583\cdot 10^6}{1800+I^{DNP}}$	pentan-2-one	105	106	103	101	101
	hexan-2-one	129	131	129	127	127.5
$T_b=582-\frac{8.56\cdot 10^5}{729+I^{PEGA}}$	heptan-2-one	151	152	151	151	151.5
	octan-2-one	171	172	172	—	173
$T_b=771-\frac{1.403\cdot 10^6}{823+I^{\beta\beta'}}$	undecan-2-one	223	224	223	—	223
$T_b=2097-\frac{1.691\cdot 10^7}{7814+I^{Ap-M}}$	pentan-3-one	103	105	104	—	101.7
	heptan-4-one	144	143	143	—	144.2
$T_b=2316-\frac{2.161\cdot 10^7}{8994+I^{DNP}}$	nonan-5-one	188	186	189	—	187.7
$T_b=707-\frac{1.253\cdot 10^6}{1022+I^{PEGA}}$	undecan-6-one	227	227	226	—	228

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* Indices determined at 125°C, except in the case of oxy-$\beta\beta'$-oxydipropionitrile (50°C).

Table 9. Comparison of boiling points of sulphur-containing compounds calculated from the retention indices $I^{\text{Ap-M}}$ with published values*.

Compound	Boiling point, °C calculated	Boiling point, °C published
Thiols		
Ethane-	35.0	35.0
Propane-	68.8	67.6
Butane-	99.5	98.5
Hexane-	153.3	151.5
Heptane-	177.5	176.2
Nonane-	220.9	220.2
Dodecane-	277.0	277.3
Propane-2-	52.4	52.6
Isopentane-	113.0	118.0
Isobutane-2-	63.9	64.2
Neopentane-	101.2	99.0
Prop-2-ene	63.6	67.5
Benzene-	169.6	168.7
Sulphides		
Dimethyl	32.8	37.3
Diethyl	92.4	92.1
Dipropyl	143.1	142.8
Dibutyl	189.0	188.9
Dipentyl	229.7	229.0
Dihexyl	266.2	260.0
Ethyl methyl	67.8	66.7
Methyl propyl	96.7	95.5
Butyl ethyl	144.4	144.2
Di-isopropyl	116.8	120.2
Di-isobutyl	168.4	170.1
Di-t-butyl	150.1	146.0
Di-isopentyl	213.4	215.2
Diallyl	134.5	138.0
Ethyl vinyl	91.5	91.5
Disulphides		
Dimethyl	110.0	109.7
Diethyl	154.0	154.0
Dipropyl	195.3	195.8
Dibutyl	233.8	235.0
Di-isopropyl	175.4	174.0
Di-t-butyl	197.5	200.5
Cyclic		
Thiophen	84.0	84.2
Thiophan	121.1	121.1
2-Methylthiophen	112.6	112.6
2,5-Dimethylthiophen	136.7	136.7

* Indices determined at 130°C.

Scheme 2

Straight-chain and isomeric thiols, sulphides, and disulphides $$T_b = 896.3 - \frac{2.255 \cdot 10^6}{I_{130}^{\text{Ap-M}} + 2106}$$

Cyclic compounds $$T_b = 899.1 - \frac{2.255 \cdot 10^6}{I_{130}^{\text{Ap-M}} + 2106}$$

Isoalkanethiols and isoalkyl disulphides $$T_b = 872.6 - \frac{2.153 \cdot 10^6}{I_{130}^{\text{OV}} + 1998}$$

Symmetrical and unsymmetrical straight-chain sulphides $$T_{\text{K}} = 726.2 - \frac{1.359 \cdot 10^6}{I_{130}^{\text{OV}} + 1356}$$

n-Alkyl and isoalkyl disulphides $$T_b = 847.3 - \frac{1.889 \cdot 10^6}{I_{130}^{\text{OV}} + 1670}$$

The identification of a multicomponent mixture from chromatograms on three or four columns is very tiresome and time-consuming. The accumulated experimental data have been used to set up a computer programme. Fig. 1 shows the logical sequence of operations involved in deciphering an analysis. The programme was set up in computer codes in collaboration with Grigor'eva and Zhuravleva[27]. Experimental values of the indices I from all the chromatograms were fed into the computer, and for each group of organic compounds the coefficients in the equations by means of which the numbers of carbon atoms n and the boiling points were determined. The data fed into the computer and their notation are given for the analysis of amines as example.

1. Series of compounds having functional groups of the same type q, where q_1 represents primary amines, q_2 secondary amines, q_3 tertiary amines, q_4 pyridine derivatives, and q_5 other amines.

2. The sequence of processing data from the columns, with i the number of the column and j the number of the peak on the chromatogram; $i = 1$–4 represent respectively tristearin, mineral oil, Tween-80, and polyethylene glycol 1000.

3. The coefficients α, σ, B, and L for the calculation of n and T_b by means of the equations

$$n = \frac{I_{ji} - B_{q_i}}{L_{q_i}}; \quad T_b = \frac{I_{ji}}{\alpha_{q_i}} - \sigma_{q_i}.$$

4. Retention indices and their differences $I_{j,i}$ and ΔI. The permissible errors in the comparison of I, ΔI, and T_b are

$$\theta_I = \pm 5\,\text{deg}; \quad \theta_T = \pm 5\,\text{deg}; \quad \theta_{\Delta I} = \pm 20\,\text{deg}.$$

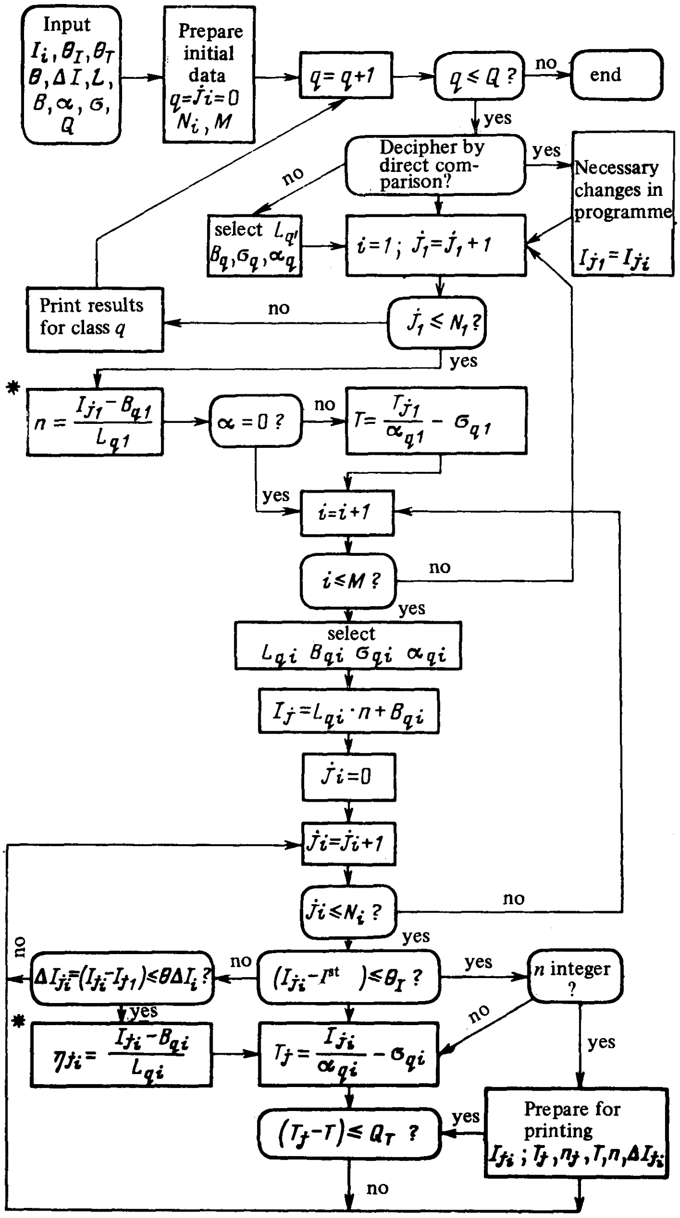

Figure 1. Block diagram of computer programme for identifying complicated mixtures from gas-chromatographic analysis without use of standard substances. For notation see text.

5. Several other parameters are also used by the computer: Q is the maximum number of series of compounds, M the maximum number of columns, and N_i the maximum number of peaks on each chromatogram. The programme permits the simultaneous processing of analytical data for a mixture of 12 types of compounds on 8 columns giving chromatograms each of which may contain up to 200 peaks[27].

The methods developed make possible the identification not only of members of the homologous series studied. In the case of unsymmetrical aliphatic and heterocyclic compounds the character of the functional group can be determined accurately, the number of carbon atoms tentatively predicted, and the boiling point of the compound estimated. The computer prints the results as a list of provisionally recognised compounds. The block scheme in Fig. 1 is of fundamental importance. It can be used to elucidate the components not only of an odour but also of other natural mixtures, e.g. hydrocarbon fractions of petroleum, essential oils, etc. The logical sequence of operations in the block diagram remains unchanged even if the gas-chromatographic behaviour of a whole series of substances on a system of columns differing in polarity is expressed in other parameters than the indices. With the accumulation of experimental information on the structural contributions to the indices the programme can be extended by calculating the indices of structures of provisionally recognised compounds. This will guide the choice of standard substance to confirm the structure of such compounds, which will facilitate identification. If the preliminary operations of calculating the indices from retention times according to previously published programmes[57] are introduced into the block diagram in Fig. 1, the task of the experimentalist is reduced to obtaining chromatograms, feeding retention times of peaks directly from the integrator into the computer, and identifying merely the peaks provisionally recognised by the computer.

V. ODOUR COMPONENTS OF CERTAIN FOODSTUFFS

Methods of identification without use of standards have been used to study the odours of several foodstuffs containing protein of animal origin—soft roe from salmon and sturgeon, salmon fillets, Russian and Dutch cheeses, volatile components of the Maillard reaction, simulating the odour of cooked meat.

The sequence of operations adopted in investigating volatile components was to obtain an odour condensate, to determine the classes of organic compounds of significance for reproducing the flavour of the product under investigation, to concentrate these classes of compounds as derivatives, to regenerate them, and then to undertake identification by gas-chromatographic analysis without the use of standard substances.

It was found that amines and monocarbonyl compounds were the most significant for the odours of sturgeon and salmon roe and of salmon fillet. The odour of cheeses is determined primarily by organic carbonyl compounds, acids, and to some extent organic bases. Sulphur-containing compounds are important in the odour of cooked meat. The results of the identification are set out in Tables 10–12.

There are several important differences in composition between the amines of sturgeon and salmon roes, and these affect their organoleptic properties. Thus the former contain more heterocyclic compounds, in particular pyridine, and the latter trimethylamine, which is characteristic of a fishy odour. It must be stressed that it has not hitherto proved possible to detect such a large number of volatile organic bases in any foodstuff. The results indicate that differences in odour between fish and fish products are probably due mainly to different quantitative relations among nitrogen bases.

Table 10. Proportions of amines in volatile components of foodstuffs expressed as relative percentages*.

Amine	Sturgeon roe	Salmon roe	Dutch cheese (4-month)	Russian cheese (4-month)	Russian cheese (10-month)
Methylamine	2.2	3.2	7.0	7.4	0.2
Dimethylamine	2.8	1.0	2.9	2.5	2.5
Trimethylamine	3.4	87.5	13.5	14.3	3.0
Ethylamine	2.5	—	—	—	0.3
Diethylamine	2.8	0.4	1.0	2.5	1.1
Triethylamine	9.0	0.3	4.6	4.8	2.8
Propylamine	12.0	—	—	0.6	—
Isopropylamine	2.0	0.1	0.5	0.2	0.1
Dipropylamine	2.6	0.3	5.5	2.9	0.5
Di-isopropylamine	8.6	2.3	8.9	9.0	8.8
Tripropylamine	—	0.1	1.5	1.2	0.1
Butylamine	3.1	0.3	1.4	—	—
Isobutylamine	—	1.8	11.8	12.8	0.5
Dibutylamine	2.4	0.3	1.9	1.2	0.4
Di-isobutylamine	1.8	0.1	1.1	0.3	0.1
Pentylamine	2.8	0.1	—	—	—
Isopentylamine	—	0.2	—	0.6	0.1
Pyridine	40.4	0.3	29.2	29.6	4.9
2-Methylpyridine	1.4	0.6	6.0	7.5	52.4
Piperidine	—	0.5	1.2	0.4	15.4
Pyrrolidine	—	0.1	0.2	—	0.2
3-Methylpyridine	—	—	—	—	0.3
Perhydroazepine	—	—	—	—	0.3
Unidentified amines	0.4	0.5	2.0	2.3	6.4

* Sum of areas of peaks of all amines, including those that remain unidentified, taken as 100%.

Lactic acid bacteria are widely used in the manufacture of various foodstuffs, and several of them are found in the alimentary canal. Investigation of the volatile components of the metabolism of such bacteria is therefore of especial interest. Analysis of the organic bases in volatile products of *Streptococcus lactis* shows that amines, including secondary and tertiary, accumulate during the logarithmic growth phase[58,59].

Comparison of the qualitative composition of the amines identified in various foodstuffs shows in all cases the presence of aliphatic amines, including secondary and tertiary, as well as heterocyclic compounds. Straight-chain amines are accompanied by many compounds containing isoalkyl groups. These results are of interest not only in the investigation of odour but also in the study of the carcinogenic nitrosamines contained in convenience meals or formed in the organism from precursors—amines and sodium nitrite.

Organic monocarbonyl compounds as well as amines have been studied in the odour condensates from the foodstuffs investigated. Table 11 lists the compounds found and their relative contents in the odour. With programming of the column temperature identification by means of my proposed equivalent isothermal index $I_{T_0/\beta}$ has revealed 4–9 additional compounds (indicated by an asterisk). Thus the formula for this index can be successfully applied to the analysis of a natural mixture of unknown composition with linear programming of the column temperature.

Table 11. Proportions (in relative percentages) of monocarbonyl compounds identified among volatile components of foodstuffs.

Compound	Sturgeon roe	Salmon roe	Salmon fillet	Russian cheese
		Alkanals		
Ethanal	4.5	2.36	3.2	5.4
Propanal	3.5	3.75	8.29	0.15
Butanal	2.8	1.65	0.44	2.0
Pentanal	38.3	0.28	5.82	0.7
Hexanal	2.4	0.82	2.14	0.95
Heptanal	0.5	1.76	0.29	0.2
Octanal	0.8	0.67	12.4	0.9
Nonanal	1.5	1.21	5.1	0.6
Decanal	1.7	0.46	1.21	0.7
Undecanal	0.06	1.21	4.52	0.12
Dodecanal	—	3.24	4.78*	—
Isobutanal	4.3	3.74	1.89	0.16
Isopentanal	6.2	33.4	0.9	1.9
		Alk-2-enals		
Propenal	4.9	1.1	0.72	3.0
Butenal	0.2	0.04	0.05	0.17
Pentenal	0.5*	0.09*	0.05*	[illegible]
Hexenal	0.07*	0.17*	0.68*	—
Heptenal	—	0.59	1.21	0.1
Octenal	1.8	0.5	0.63	0.01
Nonenal	0.1	0.13	3.96	0.13
Decenal	0.06	0.81	1.84	0.05
Undecenal	—	1.6	0.45*	—
		Alka-2,4-dienals		
Hexadienal	0.7	—	0.19	0.3
Heptadienal	0.06	0.09	0.29	0.01
Octadienal	0.07	0.07	1.03	0.04
Nonadienal	0.07	0.44	0.46	0.04
Decadienal	—	0.89	1.05*	—
		Alkan-2-ones		
Propanone	4.8	8.43	5.08	42.0
Butanone	0.7	0.44	0.26	13.7
Pentanone	12.8	1.11	3.47	5.6
Hexanone	0.4	0.16	0.08	0.3
Heptanone	0.06*	—	0.19	4.6
Octanone	0.04*	0.14	8.7	0.03
Nonanone	0.7	0.72	0.81	1.6
Decanone	0.4	0.05	5.23	0.06
Undecanone	0.1	10.73	2.82	0.5
Dodecanone	—	2.54	2.44*	—
Isopentanone	0.48	0.16	0.09	0.02
		Totals in relative %		
Alkanals	67.6	54.3	51.0	13.8
Alk-2-enals	8.3	5.1	9.6	3.5
Alk-2,4-dienals	0.9	1.5	3.0	0.4
Alkan-2-ones	20.9	24.6	29.1	68.4
Unidentified	3.2	14.6	7.3	13.8

* Further identified by means of the isothermal index obtained in gas chromatography with linear programming of the column temperature.

Comparison of the quantitative proportions of various monocarbonyl compounds in the odours showed the predominance (50–70%) of alkanals in fish products, and a relatively high content of unsaturated aldehydes in salmon fillets, whereas in the odour of cheese only 13.8% of alkanals was detected, but the quantity of alkan-2-ones reached almost 70%. This represents the first observation of so many monocarbonyl compounds in the odour of such foodstuffs.

Organic sulphur compounds have been studied in the volatile components of the Maillard reaction with the odour of cooked meat[42]. Table 12 lists 25 sulphur-containing compounds identified in the odour condensate. This is probably the first case in which a large number of organosulphur compounds have been obtained from a single amino-acid (cysteine) as source of sulphur[42]. Study of the condensate of the vapour phase from the Maillard reaction is promising from the present point of view, since it permits the examination of a smaller number of components than with odour condensates from the natural product, which contains far more compounds not involved in the formation of flavour.

Table 12. Sulphur-containing compounds identified in condensate of volatile components of the Maillard reaction.

Hydrogen sulphide
Methanethiol
Ethanethiol
Propane-1-thiol
Propane-2-thiol
Butanethiol
Neopentanethiol
Hexanethiol
Dipropyl sulphide
Di-isopropyl sulphide
Butyl propyl sulphide
Dibutyl sulphide
Butyl pentyl sulphide*
Dimethyl disulphide
Diethyl disulphide
Dipropyl disulphide
Ethyl propyl disulphide*
Di-t-butyl disulphide
Di-isobutyl disulphide
Butyl propyl disulphide*
Thiophen
2-Methylthiophen
2,5-Dimethylthiophen
Benzenethiol
2,5-Dimethyltrithiolan

* Provisionally identified.

According to the literature the odour of cooked natural meat is determined by carbonyl- and sulphur-containing organic compounds, the most significant role being assigned to thiocarbonyl derivatives[60–62]. The Reviewer's investigations have shown unambiguously that both carbonyl and thiocarbonyl compounds have only a subordinate role[42]. The presence of acids and amines is also unimportant. The odour is determined by sulphur-containing compounds.

The gas-chromatographic method of identification can be used to investigate the aroma of bread[63, 64].

VI. APPLICATION OF ODOUR ANALYSIS TO THE SOLUTION OF PRACTICAL PROBLEMS

The approach to the investigation of odour proposed and developed by the Reviewer and its application to the analysis of volatile components have enabled a simulator to be made for artificial-protein soft caviar produced in the Institute of Organoelementary Compounds of the USSR Academy of Sciences. The odour simulator was included in the technical regulations for manufacture of the caviar.

The extremely laborious investigations on the composition of the odour of natural foodstuffs can be used in solving several problems, e.g. to confer a lost flavour on products obtained by industrial methods. Thus it has been found indirectly that ethyl $\alpha\beta$-epoxy-α-methyl-β-phenylpropionate can be used in the preparation of foodstuffs smelling of strawberries. According to 1970 statistics sales in the USA were such that, if the flavouring had been natural, the size of the strawberry crop would have enabled only the demand in the single state of New Jersey to be met, although the addition of the above ester to intensify the odour was not reported to consumers[65].

Data on the composition of natural odours are used also in eliminating undesirable aftertastes with the aim of recovering valuable products for the nutrition of the population. Thus the work of Patterson in the USA revealed in 1968 the reason for the intense "smell of cats" developed in meat when stored for a long time. It was found that 0.4% of mesityl oxide contaminating the solvents for the paints previously applied to the meat-store will react with hydrogen sulphide evolved from the meat to form 4-mercapto-4-methylpentan-2-one, which has an intense "catlike" odour and a low sensitivity threshold[66,67].

Knowledge of the composition of the odour components of natural products is used in the fight against their adulteration, as well as in the manufacture of products for medical nutrition. Dietary problems in obesity and in the post-operative period can be solved by the use of flavourings and taste and odour intensifiers.

During recent years an intensive search has been made for correlations which will enable the expensive sensory assessment of the quality of foodstuffs to be replaced by objective physicochemical measurements. Such work is necessary for the establishment of objective criteria for assessing the quality of foodstuffs and for their standardisation. An example of the successful solution of this problem is provided by correlations, obtained in the Scandinavian Centre for Odour Research, for assessing the quality of canned meat from gas-chromatographic data, which required the elaboration of a verbal description of quality. Mathematical statistics was then applied to the organoleptic data, and an electronic computer used to find from these and gas-chromatographic data equations evaluating canned meat of good quality and with various defects. In this way it was shown that an objective assessment of the quality of a product can be obtained from gas-chromatographic results without the help of tasters[68-70].

Finally, data on the composition of components of the odour of natural products are required for solving the problem of flavouring new forms of food. The types of foodstuffs that supply the organism with proteins, carbohydrates, fats, vitamins, and mineral salts vary considerably and depend on the life-style, national traditions, and cultural peculiarities of each country. A unified set of foodstuffs, acceptable to all nations and peoples, cannot be envisaged in the foreseeable future. For this reason the food industry of each country is increasing its range and giving preference to forms customary in the national cuisine. The preparation of specific products of tasteless powdered protein concentrates requires both the imitation of a complex of structural and physical characteristics and a method of introducing flavourings that ensures their uniform distribution and prolonged fixation of the odour in the product.

The production of new types of food requires not only nutritional value but also a harmonious combination of texture, taste, and smell. Sour, salt, bitter, and sweet tastes can be conferred on a textured product by a combination of chemicals, e.g. common salt, citric acid, sugar, and piperine (the last isolated from pepper).

Intensifiers—natural substances minute additions of which reinforce particular taste sensations and produce a pleasant aftereffect—are used to improve taste properties. The formulae of some of them are given in Fig. 2. Since 1962 such compounds as sodium L-glutamate[71] and disodium 5'-inosinate and 5'-guanylate[72-74] have been widely used to improve the taste properties of meat and fish products, broths, vegetable courses, tomato juice, and sauces. They are able to suppress undesirable taints in the odour of foodstuffs, such as "sulphide", "greasy", "grassy", "chemical", etc. The most astonishing effect is the ability of nucleotides to create the illusion of substantiality: such sensations arise e.g. on the addition of 50–200 ppm to a broth.

Nutritionists have pointed out the unfavourable consequences of excess of carbohydrates, in particular sugar.

Addition of 15 ppm of a sweet taste intensifier—Maltol (3-hydroxy-2-methyl-4-pyrone)—enables the consumption of sugar in fruit juices and drinks to be reduced to 15%. The methyl ester of the dipeptide L-aspartyl-L-phenylalanine, which is 200 times as sweet as sugar, has also been recommended as a substitute for the latter[75].

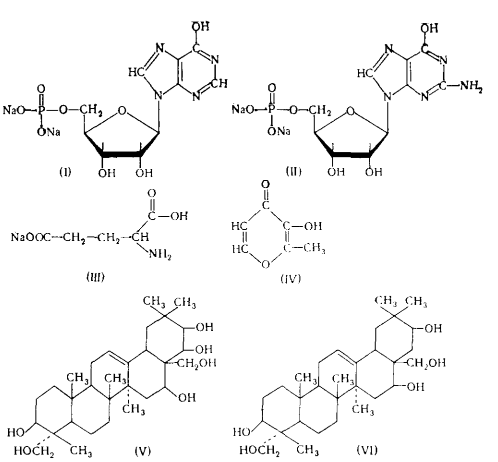

Figure 2. Some taste and odour intensifiers: (I) sodium 5'-inosinate; (II) sodium 5'-guanylate; (III) sodium glutamate; (IV) Maltol; and inhibitors: (V) gymnemagenin; (VI) gymnoestrogenin[76].

Not only taste intensifiers but also taste inhibitors have been found. For example, gymnoestrogenin[76], isolated from an African plant, suppresses a sweet taste and to some extent a bitter taste for several hours: sugar seems as tasteless as sand. The berries of the Nigerian plant *Synsepalum dilcificum* suppress a sour taste and strengthen a sweet taste (lemons taste like oranges)[77]. A thorough search is being undertaken for new inhibitors and intensifiers of taste and smell[77,78].

It is a far more complicated task to imitate the flavour of food. The creation of flavouring compositions involves deciphering the odour of natural foodstuffs. Among the several hundreds of odour components it is necessary to determine the specific, key compounds responsible for the characteristic flavour. An odour simulator for a foodstuff should be harmless and contain substances present in the flavouring composition of the natural product or obtained by reactions simulating processes occurring in the natural foodstuff (e.g. by the Maillard reaction).

The most successful examples of the conferment of odour on artificial products are provided by drinks and wines[65,79]. The reason is that flavouring compositions based on study of the odour of natural juices and wines do not change their properties on addition to aqueous and aqueous–alcoholic solutions. In this case the "texture" of the product does not appreciably affect the balance in the initial composition. Numerous attempts to impart a flavour to structured products by means of artificial compositions having a flavour closely similar to that of the natural product have given a positive result only when 95–50% of the natural product was added as foundation to the artificial product. Protein soft caviar is probably the first artificial product flavoured with an imitator without addition of the natural roe. By itself this imitation does not possess the odour of sturgeon roe, the flavour being formed in the product after introduction of the odour imitation in 2–3 h after the establishment of adsorption–desorption equilibrium[27].

The flavouring of a structurised protein usually involves a change in odour owing to disturbance of the quantitative relations among the components. Selective adsorption of the components of a flavouring mixture disturbs the quantitative proportions of the ingredients with loss of the specific odour. The selection of imitations for new forms of food may be considerably complicated by cases of synergism—the suppression or strengthening of the odour of a substance in the presence of one or more other substances—when the concentrations of the compounds may be less than the threshold values, so that each of them separately could not be perceived by man.

For two substances at concentrations x and y synergism can be expressed both as $x + y$ and as xy, and even x^y.[80] This is why the selection of flabourings cannot yet be based solely on instrumental data, but depends on the intuition and experimental skill of the chemist. Thus cases of synergism have made it extraordinarily difficult to produce a flavouring mixture for protein soft caviar, by increasing the number of variations to 200. The imitation itself does not possess the odour of roe, which appears in the culinary processing of the product and, in the opinion of tasters, imparts to protein caviar "an aromatic and gustatory character closely resembling the natural roe of fishes of sturgeon species".

A chemical imitation of an odour usually comprises 10–20 reactive compounds, which change readily not only on storage in air but also by interaction among the components. It is therefore necessary to preserve such mixtures by encapsulation or by "sealing" them into edible polymers—e.g. alginates, dextrans, polyvinyl alcohol, dextrins, etc.[81,82]—from which the components are easily displaced when required by the action of water. These powders are convenient as ingredients of products for prolonged storage. They are used also in the flavouring of fodder for cattle. In Japan, for example, special flavouring mixtures in powder form are added to improve the appetite, which promotes better anabolism of the fodder.

We may note in conclusion that the development of investigations on the odour of foodstuffs and the production of imitators are economically advantageous, despite the expensive equipment and highly qualified experts required for research on this problem. The combination of a gas-chromatographic method of separation, developed for each class of organic compounds, with mass-spectrometric detection constitutes the optimum procedure enabling maximum information to be obtained on the composition of an odour.

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Theory of Complex Unimolecular Reactions

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A general approach to the study of complex reacting systems, including first-order reactions, is considered. The method consists in the identification of the disposition of the characteristic vectors of the kinetic matrix for a linear system and their eigenvalues. Linear reaction pathways in the composition space correspond to non-equilibrium characteristic vectors. For an experimental determination of the kinetic constants in a complex system, it is sufficient to find all the linear reaction pathways.

The bibliography includes 56 references.

CONTENTS

I. INTRODUCTION

The theory of complex reactions deals with the general characteristics of their occurrence, i.e. the structural features of complex systems. Suppose that a system of non-linear differential equations describing the kinetics of a process has been specified:

$$\frac{da_i}{dt} = f_i(a_1 \ldots a_n); \quad i=1, \ldots n, \tag{1}$$

where a_i are the reactant concentrations and t is the time. The theory of steady-state reactions is concerned with problems of deriving kinetic equations from the steady-state condition:

$$f_i(a_1 \ldots a_n) = 0. \tag{2}$$

These problems were described in detail by Temkin, Kiperman, and Horiuti[1-5] and are not considered in the present review. Only a few general results have been obtained for the non-linear system (1). They are mainly restricted to the development of methods for the integration of the equations in specific instances and the consideration of methods for the determination of kinetic constants from experimental data—by analysing the number and stability of steady states. However, all these results are fairly specific.

Complex systems of unimolecular reactions have been investigated most fully. It is now already possible to describe in fair detail the structure of linear systems. A general method for the determination of the rate constants for individual pathways can be proposed on the basis of a theoretical analysis of experimental data. The new approach to the determination of first-order rate constants is based on finding "linear pathways" in the reaction, which will be discussed in detail below.

The present review considers mainly the general results of the theory of linear systems with a subsequent brief discussion of second-order reactions.

II. THEORY OF FIRST-ORDER REACTIONS

1. FUNDAMENTAL CONCEPTS AND NOTATION

We shall denote the ith substance in the system by A_i and its concentration by a_i. k_{ij} is defined as the rate constant for the conversion of the ith substance into the jth substance, i.e. we shall write $A_i \xrightarrow{k_{ij}} A_j$. We introduce a linear composition space, the dimensions of which are the same as the number of reactants. The elements of this space consist of vectors, whose coordinates are the same as the concentrations of the components at the outlet from the reactor: $a = \begin{pmatrix} a_1 \\ \vdots \\ a_n \end{pmatrix}$. The general system of first-order reactions can then be described by the following equation in the matrix form:

$$\frac{da}{dt} = Ka \quad , \qquad (3)$$

where K is the kinetic matrix. The form of this matrix depends on the specific reaction mechanism.

We shall attempt to answer two main questions concerning the general theory of first-order systems.

1. We shall elucidate the nature of the approach of the system to equilibrium, the possibility of decaying and non-decaying oscillations.

2. We shall attempt to devise a general method for the determination of rate constants from experimental data by studying the structure of the system.

The formulation of the first problem does not require special comment. We shall note only that the stability of the system is inferred from the sign of the real root of the characteristic equation

$$|K - \lambda E| = 0, \qquad (4)$$

where E is the unit matrix. If all the roots are real and negative, the system is stable and oscillations are impossible. If the roots are complex with a negative real component, decaying oscillations are possible.

The problem of the determination of kinetic constants will be considered in somewhat greater detail. The determination of constants for a system of complex reactions is known to involve considerable difficulties[6,7]. The constants for system (1) can be determined from the initial rates of formation of each substance. However, this entails significant errors in the determination of contact times and also errors in chemical analysis for low degrees of conversion[6]. It is possible to obtain a general solution to Eqns. (3),[8] but this hardly facilitates the determination of kinetic constants from experimental data. The point is that each kinetic curve can be described by an expression of the type

$$a_i = \sum_{i=1}^{n} c_i e^{\lambda_i t},$$

where c_i are constant and λ_i are the roots of the characteristic equation. It is therefore possible to obtain only c_i and λ_i from the experimental data. This is also not a simple problem, which has to be solved by non-linear programming methods[9]. A new method has been proposed recently for the determination of these quantities, which is apparently useful in the simplest cases[10]. The method is based on the fact that the function

$$\varphi = \sum_{i=1}^{n} a_i t \, e^{\lambda_i t}$$

has n maxima at the points $t_i = -1/\lambda_i$. It is therefore possible to find λ_i by plotting φ against t. However, it is difficult to expect the method to be applicable when $n > 3$ or 4. We shall assume that we have nevertheless succeeded in determining c_i and λ_i. The relation between the λ_i and the kinetic constants is so complex that an accurate determination of the latter is still a problem. A number of studies have been made on the analysis of the errors arising in the determination of the contact time and temperature[6,11-15]. Owing to the inaccuracy of the temperature measurements, the errors in the calculation of the rate constants are higher for larger activation energies. When the relative rate constants are determined, the error associated with the inaccurate determination of the constants diminishes, since the rate constant ratios depend less on temperature than the absolute values of the constants.

The approach to the problem of the calculation of the constants, based on the study of the structure of a system of unimolecular reactions, is of considerable interest[16]. Using this approach, it is possible to suggest a method for the determination of the relative rate constants without measuring contact times.

2. REVERSIBLE REACTIONS

We shall begin the consideration of systems of unimolecular reactions with first-order reversible reactions. The structure of such systems is simpler than the structure of systems including irreversible stages, despite the fact that a larger number of constants is required for the description of reversible reactions. The causes of this at first sight paradoxical fact will be clarified by further exposition.

In order to permit a simple geometrical interpretation of the results, we shall restrict the treatment initially to a three-component system. The following kinetic equations can be formulated:

$$\begin{aligned} \frac{da_1}{dt} &= -(k_{21}+k_{31})\,a_1 + k_{12}a_2 + k_{13}a_3, \\ \frac{da_2}{dt} &= k_{21}a_1 - (k_{12}+k_{32})\,a_2 + k_{23}a_3, \\ \frac{da_3}{dt} &= k_{31}a_1 + k_{32}a_2 - (k_{13}+k_{23})\,a_3. \end{aligned} \qquad (5)$$

In this case the matrix K can be written thus:

$$K = \begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & k_{13} \\ k_{21} & -(k_{12}+k_{32}) & k_{23} \\ k_{31} & k_{32} & -(k_{13}+k_{23}) \end{pmatrix}. \qquad (6)$$

The column matrix $a = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$ can be imagined as a vector in a three-dimensional composition space. During the reaction, the vector a migrates in the space. The matrix

$$\frac{da}{dt} = \begin{pmatrix} \frac{da_1}{dt} \\ \frac{da_2}{dt} \\ \frac{da_3}{dt} \end{pmatrix}$$

specifies the rate of this migration. The trajectory of the end of the vector a will be called the reaction pathway.

For an n-component system, the form of the matrix K remains the same, i.e. the non-diagonal elements consist of the rate constants for the corresponding transitions. The diagonal elements consist of sums of the elements of each column with the sign reversed. The constants k_{ii} are disregarded, since they have no physical significance.

We impose two restrictions:

$$\sum_{i=1}^{n} a_i = 1; \tag{7}$$

$$a_i > 0. \tag{8}$$

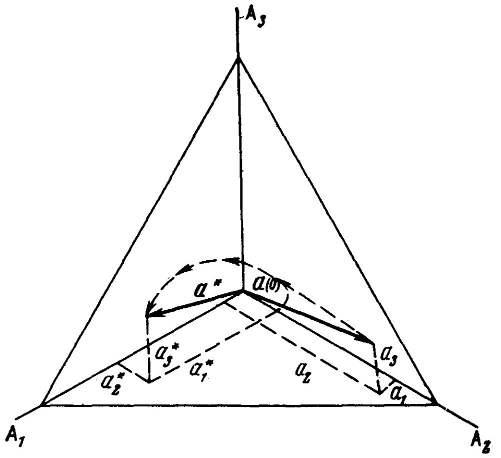


Figure 1. The composition space and the reaction triangle for a three-component system. The dashed curve represents a typical reaction pathway.

The first expresses the law of conservation of mass in the system and the second expresses the impossibility of the appearance of negative amounts of the substance.

Definition 1. The vector $a(a_1 \ldots a_n)$ is said to be positively defined if $a_i > 0$ ($i = 1, \ldots, n$); on the other hand, if $a_i \geqslant 0$ ($i = 1, \ldots, n$), then the vector a is said to be non-negatively defined. The geometrical implication of these conditions is that the end of the vector a is bounded by a plane passing through the points (1, 0, 0), (0, 1, 0), and (0, 0, 1). Furthermore, all the reaction pathways lie in the positive octant of the coordinate system (Fig. 1). During the reaction, the end of the vector $a(t)$ moves along the reaction plane in the direction towards the equilibrium point a^*. In the general case, these reactions pathways are curved.

A. Characteristic Directions

The directions in the composition space for which the condition

$$K\bar{a} = \lambda\bar{a} \tag{9}$$

is valid are called characteristic. Here a is the characteristic vector corresponding to the eigenvalue λ. It will be shown below that a linear reaction pathway corresponds to each characteristic direction.

It is known from linear algebra[17] that there can exist not more than n independent eigenvectors for an arbitrary matrix K. In terms of the coordinate system comprising eigenvectors, the matrix assumes the simplest form. If n independent eigenvectors exist (complete system), the matrix is reduced to a diagonal form. The introduction of an equivalent system of substances, each of which reacts independently of the others in the mixture, corresponds to the reduction of the kinetic matrix to the diagonal form. Evidently the calculation of constants for such a system does not present difficulties. If the eigenvectors and eigenvalues are known, it is possible to devise a transformation relating the characteristic coordinate system to the initial system. In this case, one can calculate the entire initial rate constant matrix. If the λ_i are known, then, as stated above, it is also possible to deduce the stability of the system. The study of linear reaction pathways is therefore of considerable interest for the understanding of the structure of complex systems.

The existence of a complete system of real eigenvectors for symmetrical matrices has been demonstrated in linear algebra. In the majority of instances, kinetic matrices are not symmetrical. It is therefore impossible to reach any conclusions concerning the number of eigenvectors of kinetic matrices directly on the basis of conditions (7) and (8). For reversible reactions, the kinetic matrix can be reduced to a symmetrical form. This is done using the principle of "detailed balance".

B. The Principle of Detailed Balance

This principle is important in the theory of linear systems. It states that, for each stage at equilibrium, we have

$$k_{ji}a_i^* = k_{ij}a_j^*, \tag{10}$$

and that $\varkappa_{ij} > 0$ implies that $\varkappa_{ji} > 0$.

We may note that the principle of detailed balance cannot always be obtained from the steady-state condition. For example, for the three-component system of reversible reactions considered above, one cannot obtain Eqn. (10) from the equality

$$Ka^* = 0 \tag{11}$$

without additional conditions. For $n = 2$, Eqn. (10) always follows from Eqn. (11), but for $n = 3$ this is the case only provided that the Wegsheider conditions are fulfilled[18]:

$$k_{12}k_{23}k_{31} = k_{21}k_{32}k_{13}. \tag{12}$$

For $n > 3$, analogous conditions have been obtained by other investigators[19,20]. The general conditions for which the principle of detailed balance follows from steady-state equations have been obtained by Lee[21]. For reversible reactions in closed systems, the validity of Eqn. (10) can be proved from thermodynamic considerations. However, it has been noted in the literature that, in relation to kinetics, the thermodynamic derivation of the principle of detailed balance is not always rigorous, since it is difficult to take into account multistage reaction mechanisms and deviations from ideality[22]. In the present section, we shall assume that condition (10) is valid.

C. Axiomatic Definition of a System of Unimolecular Reversible Reactions

We shall now formulate an exact definition of a system of reversible reactions and shall discuss certain mathematical results obtained from this definition.

Definition 2. A system described by the equations

$$\frac{d\boldsymbol{a}}{dt} = K\boldsymbol{a}, \quad \boldsymbol{a}(0) = \boldsymbol{a}_0, \tag{13}$$

where $\boldsymbol{a}$ is an n-dimensional composition vector and K an $n \times n$ matrix, is called a system of unimolecular reversible reactions. Furthermore, the following conditions are fulfilled:

$$\begin{gathered} a_i \geqslant 0, \\ \sum_{i=1}^{n} a_i = \text{const}, \\ k_{ij}a_j^{\bullet} = k_{\ i}a_i^{\bullet}, \end{gathered} \tag{14}$$

where a_j^* and a_i^* are equilibrium concentrations.

Theorem 1. For a system of unimolecular reversible reactions, there is a unique equilibrium point.

Theorem 2. For a system of reversible unimolecular reactions, there are n independent characteristic composition vectors, whose eigenvalues are not positive.

The proof of theorem 2 is based significantly on the principle of detailed balance [condition (14)]. The idea of the proof is as follows. Knowing the equilibrium composition, it is possible to set up the diagonal matrices

$$D^{-1/2} = \begin{vmatrix} \frac{1}{\sqrt{a_1^{\bullet}}} & & \\ & \ddots & \\ & & \frac{1}{\sqrt{a_n^{\bullet}}} \end{vmatrix}; \quad D^{1/2} = \begin{pmatrix} \sqrt{a_1^{\bullet}} & & \\ & \ddots & \\ & & \sqrt{a_n^{\bullet}} \end{pmatrix}. \tag{15}$$

These matrices are evidently non-degenerate. We now consider the trans-formation of the vector composition space in accordance with the formula $\alpha = D^{-1/2}\boldsymbol{a}$. Here we again obtain a system of reversible unimolecular reactions:

$$\frac{d\alpha}{dt} = \hat{K}\alpha, \tag{16}$$

where $\hat{K} = D^{-1/2}KD^{1/2}$. By virtue of conditions (14), the matrix $\hat{K}$ is symmetrical, as a result of which it has n independent eigenvectors. Theorem 2 is now confirmed by the similarity of matrices K and $\hat{K}$.

The non-positive nature of the eigenvalues leads to a corollary.

Corollary 1. In a system of unimolecular reversible reactions, oscillations are impossible.

The characteristic vectors of a symmetrical matrix are linked by orthogonality relations. Since these relations will be used below to find the characteristic vectors, we may also note another corollary.

Corollary 2. The characteristic vectors $X_j(x_{j1}, \ldots, x_{jn})$ of the matrix K are linked by relations of the type

$$(X_j, D^{-1} \cdot X_i) = 0, \tag{17}$$

where the brackets indicate a scalar product and the matrix D^{-1} is defined thus:

$$D^{-1} = \begin{Vmatrix} \frac{1}{a_1^{\bullet}} & & \\ & \ddots & \\ & & \frac{1}{a_n^{\bullet}} \end{Vmatrix}. \tag{18}$$

D. Solution for a First-Order Reaction System in Terms of the Concentrations of the Characteristic Substances

We saw above that there exist n characteristic composition vectors in the composition space for a system of reversible unimolecular reactions. Suppose that the unit characteristic vector in the initial coordinate system is designated by X_i. We select the unit vectors X_i as the new coordinate system. We shall refer to the system as the characteristic system or the system of equivalent substances B. Any composition vector can be written in the form

$$\alpha = \sum_{i=0}^{n-1} b_i(t)X_i. \tag{19}$$

When α is substituted in the initial equation (3), we obtain

$$\frac{d\alpha}{dt} = \sum_{i=0}^{n-1} \frac{db_i}{dt} X_i = K\alpha = \sum_{i=0}^{n-1} b_i(t) \cdot \lambda_i X_i,$$

whence

$$\frac{db_i}{dt} = \lambda_i b_i, \quad \lambda_i \leqslant 0. \tag{20}$$

The solution of Eqn. (20) presents no difficulties:

$$b_i(t) = b_i^0 e^{\lambda_i t}; \quad i = 0, \ldots n-1. \tag{21}$$

If $\lambda_i < 0$, then $b_i(t) \to 0$ when $t \to \infty$. Substitution of $b_i(t)$ defined by Eqn. (21) in Eqn. (19) yields

$$\alpha = \sum_{i=0}^{n-1} b_i^0 e^{\lambda_i t} X_i. \tag{22}$$

Since material balance must hold, then at least one eigenvalue should be zero. We shall denote it by λ_0. Then

$$\alpha = b_0^0 X_0 + \sum_{i=1}^{n-1} b_i^0 e^{\lambda_i t} X_i. \tag{23}$$

Since the sum of the concentrations of the components at any instant is unity, we obtain

$$\sum_{j=1}^{n} \alpha_j = b_0^0 \sum_{j=1}^{n} x_{0j} + \sum_{i=1}^{n-1} b_i^0 e^{\lambda_i t} \cdot \sum_{j=1}^{n} x_{ij} \equiv 1. \tag{24}$$

It follows from Eqn. (24) that $\sum_{j=1}^{n} x_{ij} = 0$ and that the following relation holds when the length X_0 is suitably chosen

$$\sum_{j=1}^{n} x_{0j} = 1. \tag{25}$$

Evidently there exists only one positively defined characteristic composition vector X_0 in the system. All other characteristic vectors contain negative elements, since otherwise the equality $\sum_{j=1}^{n} x_{ij}=0$ would have been impossible. Geometrically this condition implies that the characteristic vectors are perpendicular to the vector $I\{1, 1, 1\}$. For a three-dimensional system, the vectors $X_i (i \neq 0)$ are parallel to the plane of the reaction triangle. Since the vectors X_i contain negative coordinates, linear reaction pathways directed along these vectors cannot be observed experimentally. A significant feature of reversible reactions is that at equilibrium the system contains all the substances for which the equilibrium characteristic vector X_0 does not have zero coordinates. One can therefore always find a linear combination of X_0 and X_i such that the resultant vector is non-negatively defined.

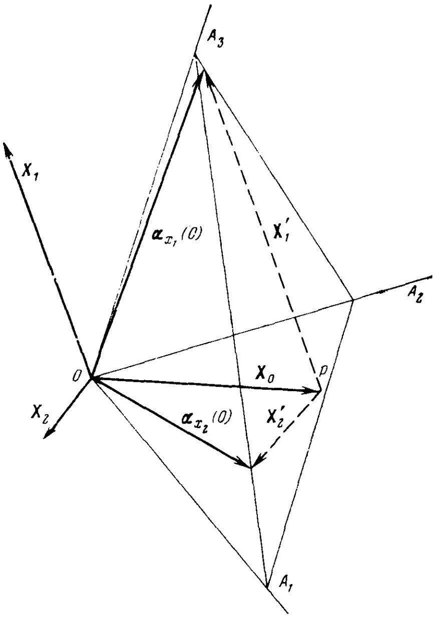


Figure 2. Disposition of the characteristic vectors for a three-component system. The dashed lines represent the characteristic vectors transferred to the equilibrium point P.

We now turn to the geometrical interpretation for a three-component system. Since the vectors X_1 and X_2 are parallel to the plane of the reaction triangle and during the reaction move to the equilibrium point P (Fig. 2) located in the plane of the reaction triangle, one may assert that the vectors X_1 and X_2 lie in this plane. We have not so far refined the lengths of the vectors X_1 and X_2 which are the unit vectors in the system B. We shall choose them in such a way that their ends are located on the sides of the reaction triangle. The vector sums

$$\alpha_{x_1}(0)=X_0+X_1 \text{ and } \alpha_{x_2}(0)=X_0+X_2 \tag{26}$$

then correspond to real compositions.

Definition 3. The characteristic vectors $X_i (i \neq 0)$ satisfy Eqn. (26), where X_0 is a positively defined vector and $\alpha_{x_1}(0)$ a non-negatively defined vector, will be called quasipositive. At least one element of each vector $\alpha_{x_i}(0)$ is zero owing to the above choice of the length of the vectors X_i, which restricts $\alpha_{x_i}(0)$ to the area bounded by the reaction triangle.

Eqns. (26) are equivalent to Eqns. (22) for $n = 3$, $b_0^0 = b_1^0 = 1$, $b_2^0 = 0$ or $b_0^0 = b_2^0 = 1$, $b_1^0 = 0$. Using Eqns. (22) and (26), we obtain equations for the migration of $\alpha_{x_1}(t)$ and $\alpha_{x_2}(t)$ towards equilibrium:

$$\alpha_{x_1}(t)=X_0+e^{\lambda_1 t}X_1, \tag{27}$$

$$\alpha_{x_2}(t)=X_0+e^{\lambda_2 t}X_2. \tag{28}$$

Eqns. (27) and (28) define linear reaction pathways in the composition space. They show that

$$X_l=\alpha_{x_l}(0)-X_0. \tag{29}$$

Thus, in order to determine the characteristic vectors, it is necessary to know the points of intersection of the linear reaction pathways with the sides of the reaction triangle and the equilibrium composition vector. The problem of the determination of the eigenvectors has been reduced to finding the linear reaction pathways. The eigenvectors are fully defined within the composition space and their determination does not require the knowledge of the reaction time.

E. Method for the Determination of Rate Constants from Experimental Data

The following method has been proposed for the experimental determination of linear pathways. We select any convenient initial composition and determine the corresponding reaction pathway. Fairly close to equilibrium, the reaction pathway is determined by the characteristic vector with the lowest eigenvalue. Linear extrapolation of the section of the pathway near equilibrium yields a new initial composition. This process is repeated until the reaction pathway becomes linear. Having eliminated the time t from Eqns. (21), we obtain

$$\ln b_i=\text{const}+\left(\frac{\lambda_i}{\lambda_j}\right)\ln b_j. \tag{30}$$

By determining the compositions along two linear sections, it is possible to find b_i and b_j and then λ_i/λ_j from the slope of the linear plot of $\ln b_i$ against $\ln b_j$. The matrix X can be set up using the coordinates of the characteristic vectors and the eigenvalues can be used to obtain the diagonal matrix Λ.

These data are sufficient to determine the relative rate constants from the relation

$$K=X\Lambda X^{-1} \quad . \tag{31}$$

The inverse of a matrix X^{-1} can be calculated as follows[16]. One evaluates initially the diagonal matrix L from the formula

$$L=X^{T}D^{-1}X, \tag{32}$$

where X^T is the transpose of a matrix. After this, the inverse of a matrix can be calculated from the equation

$$X^{-1}=L^{-1}X^{T}D^{-1}. \tag{33}$$

The graphical method, which is convenient for a three-component system, is virtually inapplicable to a system with a larger number of components. In this case, the reaction pathway can be conveniently specified in a parametric form having selected as the parameter the concentration a_j of one of the components (which varies monotonically with time). For an n-component system, there are $n-1$ equations of the type

$$a_{x_l}(t) = X_0 + e^{\lambda_l t} X_l, \tag{34}$$

corresponding to linear reaction pathways. We shall consider the linear pathway corresponding to the lth characteristic vector and shall formulate equations which follow from Eqn. (34):

$$\begin{aligned} a_1 &= x_{10} + e^{\lambda_l t} x_{1l}, \\ a_2 &= x_{20} + e^{\lambda_l t} x_{2l}, \\ &\dots\dots\dots\dots\dots \\ a_n &= x_{n0} + e^{\lambda_l t} x_{nl}. \end{aligned} \tag{35}$$

If t is eliminated with the aid of the jth equation from the remaining equations, we obtain $n-1$ equations of the type

$$a_m = \left(\overset{\bullet}{a}_m - \frac{x_{ml}}{x_{jl}} \overset{\bullet}{a}_j \right) + \frac{x_{ml}}{x_{jl}} a_j. \tag{36}$$

Thus the linear pathway in the $(n-1)$-dimensional space is converted into $n-1$ straight lines in two-dimensional spaces. The method of approximations described above for $n = 3$ can be applied also to the general case with two-dimensional representations of the reaction pathways.

For n-component systems, one must bear in mind that, after the linear pathway corresponding to the characteristic vector X_j has been found, the new initial composition used to find the vector X_{j+1} cannot be selected arbitrarily. The point is that, for certain initial compositions, the method of approximations can lead to the same linear reaction pathway. To prevent this, the initial composition is chosen in such a way that the vector $[X_0 - a(0)]$ in the system B is orthogonal with respect to X_j. The procedure will be elucidated in detail in relation to the example described below.

F. Pseudounimolecular Systems of Heterogeneous Catalytic Reactions

We considered above unimolecular reactions only. However, there exists an important class of non-linear systems for which the above results are valid. Consider a pseudounimolecular system of reactions, which will be referred to as the reaction system, where the rate of change of the amounts of various substances is expressed as first order by the law of mass action, each term of the equation being multiplied by the same function of composition and time. For example, heterogeneous first-order reactions occurring on the homogeneous catalyst surface are pseudounimolecular. For the simplest mechanism of reversible reactions A ⇌ B, one can write

$$\frac{dc_A}{dt} = -(k_1 c_A - k_2 c_B)\,\varphi(c_A, c_B), \tag{37}$$

$$\frac{dc_B}{dt} = (k_1 c_A - k_2 c_B)\,\varphi(c_A, c_B), \tag{38}$$

where

$$\varphi(c_A, c_B) = \frac{1}{1 + c_A b_A + c_B b_B}. \tag{39}$$

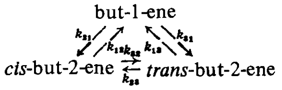
It was shown above that the matrix of the relative rate constants can be determined using only the information about the compositions and disregarding the reaction time. It is therefore possible to reduce pseudounimolecular reactions to the case analysed above by introducing a new time scale. For this purpose, we shall assume that $\varphi[c_A(t), c_B(t)]$ is a function of time and shall replace the independent variable:

$$d\tau = \varphi(t)\,dt, \tag{40}$$

which yields a system of unimolecular reactions.

G. Examples of the Determination of the Rate Constants for Reversible Unimolecular Reactions

Example 1. We shall consider initially a three-component system. The isomerisation of butenes on alumina has been investigated by Haag and Pines[23]. If it is assumed that the catalyst surface is homogeneous, the system may be regarded as pseudounimolecular. The method described above has been used[16] to calculate the rate constants. The designation of the rate constants is indicated in the scheme below:



(I)

Fig. 3 illustrates the reaction pathway obtained when pure *cis*-but-2-ene is introduced into the reactor. The dashed line represents the tangent to the curved reaction pathway drawn near the equilibrium point. The intersection of the tangent with the side of the triangle yields a new initial composition:

$$\alpha(0) = \begin{pmatrix} 0.24 \\ 0.76 \\ 0 \end{pmatrix}.$$

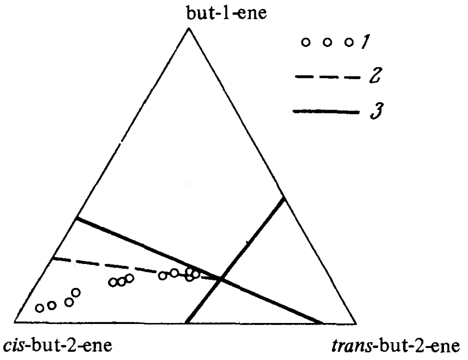


Figure 3. The study of the isomerisation of butenes in the presence of Al_2O_3: 1) reaction pathway obtained following the introduction of pure *cis*-but-2-ene into the reactor; 2) tangent to the reaction pathway; 3) linear pathways.

The sequence of components in the column matrix is

$$\begin{pmatrix} \text{but-1-ene} \\ \textit{cis}\text{-but-2-ene} \\ \textit{trans}\text{-but-2-ene} \end{pmatrix}.$$

Next, experiments were performed with the new initial composition. Table 1 presents the last twelve points forming an approximately linear section in the vicinity of equilibrium. A straight line passing through these points and the equilibrium point was fitted by the method of least squares:

$$\alpha^{*}=X_0=\begin{pmatrix}0.1436\\0.3213\\0.5351\end{pmatrix}\ .$$

Table 1. Series of compositions for the second approximation in the isomerisation of butenes.

But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene	But-1-ene	*cis*-But-2-ene	*trans*-But-2-ene
0.1622	0.3604	0.4775	0.1537	0.3471	0.4992
0.1776	0.3769	0.4455	0.1571	0.3464	0.4965
0.1664	0.3595	0.4741	0.1542	0.3431	0.5027
0.1654	0.3622	0.4724	0.1521	0.3451	0.5028
0.1690	0.3671	0.4639	0.2525	0.3408	0.5067
0.1603	0.3441	0.4955	0.1532	0.3416	0.5052

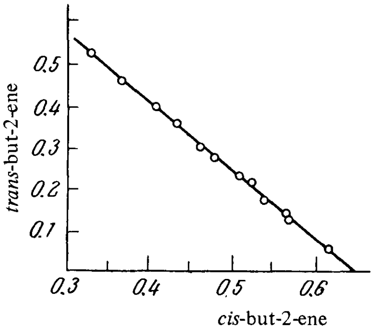


Figure 4. The linear reaction pathway in the isomerisation of butenes.

Its extrapolation to the side of the triangle yielded a new initial composition:

$$\alpha'(0)=\begin{pmatrix}0.3286\\0.6714\\0.0000\end{pmatrix}.$$

Fig. 4 presents the composition points for the reaction pathway corresponding to the last initial composition in the fourth approximation. This composition,

$$\alpha(0)=\begin{pmatrix}0.3492\\0.6508\\0.0000\end{pmatrix}$$

was used to determine the vector X_1. Using $\alpha(0)$ and X_0, we obtain

$$X_1=\alpha(0)-X_0=\begin{pmatrix}0.2056\\0.3295\\-0.5351\end{pmatrix}.$$

Calculation of the third characteristic vector. The vector X_2 may be calculated without additional measurements using the orthogonality relations (17). In our case the matrices $D^{1/2}$ and $D^{-1/2}$ are

$$D^{1/2}=\begin{pmatrix}0.3789&0&0\\0&0.5668&0\\0&0&0.7315\end{pmatrix},$$

$$D^{-1/2}=\begin{pmatrix}2.6389&0&0\\0&1.7642&0\\0&0&1.3670\end{pmatrix}\ .$$

We calculate the vectors

$$\overline{X}_0=D^{-1/2}X_0=\begin{pmatrix}0.3789\\0.5668\\0.7315\end{pmatrix}$$

$$\overline{X}_1=D^{-1/2}X_1=\begin{pmatrix}0.5426\\0.5812\\-0.7315\end{pmatrix}.$$

$\overline{X}_1$ is adjusted to unit length:

$$l_1=(\overline{X}_1,\overline{X}_1)=1.1673\ .$$

The round brackets indicate a scalar product.

$$\overline{X}_1/\sqrt{l_1}=\begin{pmatrix}0.5022\\0.5380\\-0.6771\end{pmatrix}.$$

The vector X_2 is orthogonal with respect to $\overline{X}_0$ and $\overline{X}_1$. We take initially the vector $\overline{\gamma}_1$, orthogonal with respect to X_0; this can be readily done, for example, by interchanging the first two elements of X_0, reversing the sign of one of them, and setting the third equal to zero:

$$\overline{\gamma}_1=\begin{pmatrix}-0.5668\\0.3789\\0.0000\end{pmatrix}.$$

We shall now seek $\overline{\gamma}_2$ in the form of a linear combination of $\overline{X}_1$ and $\overline{\gamma}_1$:

$$\overline{\gamma}_2=\overline{X}_1+\lambda\overline{\gamma}_1.$$

From the condition that $\overline{X}_2$ and γ_1 are perpendicular, it is easy to find that

$$\lambda=-\frac{1}{(\overline{\gamma},\overline{X}_1)};$$

$$\overline{\gamma}_2=\overline{X}_1-\frac{\overline{\gamma}}{(\overline{\gamma}_1,\overline{X}_1)}=\begin{pmatrix}-0.5262\\0.4224\\-0.0547\end{pmatrix}.$$

We now retransform $\overline{\gamma}$ so that it applies to a non-orthogonal system:

$$\gamma_2=D^{1/2}\overline{\gamma}_2=\begin{pmatrix}-0.1994\\0.2394\\-0.0400\end{pmatrix}.$$

The vectors γ_2 and X_2 are parallel. The length of X_2 is chosen so that the first coordinate of the vector $X_2+X_0=\alpha_{X_2}(0)$ is zero:

$$X_2=\begin{pmatrix}-0.1436\\0.1724\\-0.0288\end{pmatrix}.$$

We now find

$$\alpha_{x_2}=X_2+X_0=\begin{pmatrix}0.0000\\0.4937\\0.5063\end{pmatrix}.$$

On combining the vectors X_0, X_1, and X_2, we obtain the matrix

$$X=\begin{pmatrix}0.1436 & 0.2056 & -0.1436\\ 0.3219 & 0.3295 & 0.1724\\ 0.5351 & -0.5351 & -0.0288\end{pmatrix}.$$

Calculation of the inverse of a matrix. The matrix D^{-1} will be determined from the equilibrium amounts:

$$D^{-1}=\begin{pmatrix}6.9638 & 0 & 0\\ 0 & 3.1123 & 0\\ 0 & 0 & 1.8688\end{pmatrix}.$$

We calculate the matrix

$$L=X^{\mathrm{T}}D^{-1}X=\begin{pmatrix}1.000 & 0 & 0\\ 0 & 0.8566 & 0\\ 0 & 0 & 4.2077\end{pmatrix}.$$

The inverse of the matrix is found from the equation

$$X^{-1}=L^{-1}X^{\mathrm{T}}D^{-1}=\begin{pmatrix}1.000 & 1.000 & 1.000\\ 1.2265 & 0.8784 & -0.8560\\ -4.2077 & 2.2579 & -0.2269\end{pmatrix}.$$

Experimental determination of the ratios of the characteristic roots and calculation of the matrix of the relative rate constants. We now transform the reaction pathway for pure *cis*-but-2-ene so that it applies to the system B by means of the formula $\beta = X^{-1}\alpha$. The results of the recalculation are presented in Table 2.

Table 2. Isomerisation of butene.

t	$\alpha(t)$	$\beta(t)$	t	$\alpha(t)$	$\beta(t)$
t_0	0.0000 1.0000 0.0000	1.0000 0.8784 2.2579	t_3	0.1411 0.6487 0.2102	1.000 0.5629 0.8233
t_1	0.0543 0.8897 0.0560	1.0000 0.8001 1.7677	t_4	0.1620 0.5230 0.3150	1.0000 0.3883 0.4279
t_2	0.0854 0.8177 0.0969	1.000 0.7400 1.4650			

Fig. 5 illustrates the variation of $\ln b_1$ with $\ln b_2$. Evidently Eqn. (30) yields a straight line whose slope can be used to find the ratio of the characteristic roots λ_1/λ_2. Having determined $\lambda_1/\lambda_2 = 0.4769$ from the graph, we obtain the matrix:

$$\Lambda'=\begin{pmatrix}0.0000 & 0.0000 & 0.0000\\ 0.0000 & -0.4769 & 0.0000\\ 0.0000 & 0.0000 & -1.0000\end{pmatrix}.$$

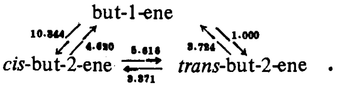
The matrix K^1 is calculated from the formula

$$K^1=X\Lambda'X^{-1}=\begin{pmatrix}-0.72 & 0.2381 & 0.0515\\ 0.5327 & -0.5273 & 0.1736\\ 0.1918 & 0.2982 & -0.2251\end{pmatrix}.$$

The matrix of the relative rate constants K can now be readily evaluated after dividing all the elements by 0.0515:

$$K=\begin{pmatrix}-14.068 & 4.623 & 1.000\\ 10.344 & -10.239 & 3.371\\ 3.724 & 5.616 & -4.371\end{pmatrix}.$$

Thus the relative rate constants are



(II)

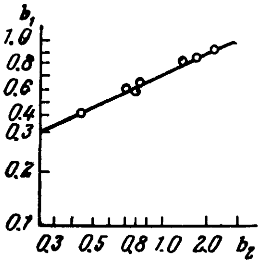


Figure 5. Variation of $\ln b_1$ with $\ln b_2$ for pure *cis*-but-2-ene as the initial species. The slope of the straight line is 0.4769.

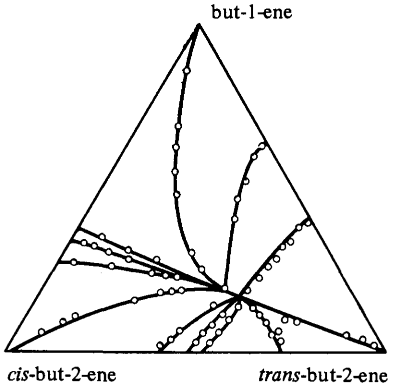
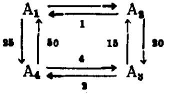


Figure 6. Comparison of the calculated reaction pathways (continuous lines) with the experimental compositions (circles) for the isomerisation of butenes.

Fig. 6 illustrates the comparison of the calculated and experimental reaction pathways.

Example 2. We shall now examine a hypothetical four-component system to which the following scheme corresponds:



(III)

Subsequently "experimental" data were obtained[16] by calculation from the exact characteristic vectors and roots based on scheme (III). Errors obeying the normal distribution for the standard deviation $\sigma = 1\%$ were added to the exact compositions.

The pure substance A was used as the initial composition. Nine "experimental compositions" along the reaction pathway were used to plot a_m against a_j in Fig. 7. The equilibrium values are located on the vertical dashed line on the left-hand side. The Figure also shows the linear approximations for each curve near equilibrium. The tangents have been produced to the a_1 axis. A vertical line is drawn from the point of intersection with the a_1 axis (corresponding to the substance A_2) nearest to the origin of coordinates. The ordinates of the intercepts of the tangents with this straight line form the matrix

$$\begin{pmatrix}0.3274\\0.0000\\0.0397\\0.6329\end{pmatrix}.$$

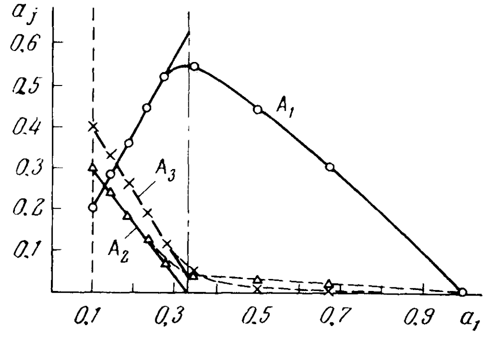


Figure 7. Method for the determination of the new initial composition in the search for a linear reaction pathway in a four-component system.

The sum of the elements of this matrix is 0.008 owing to random errors. In order to obtain a new composition, we therefore divide the matrix elements by 1.008:

$$\alpha_{x_1'}(0)=\begin{pmatrix}0.3248\\0.0000\\0.0394\\0.6279\end{pmatrix}.$$

The above procedure was then repeated until a sufficiently close agreement was obtained between successive values found on extrapolation. This yielded the matrix

$$\alpha_{x_1}(0)=\begin{pmatrix}0.3214\\0.0000\\0.0382\\0.6404\end{pmatrix}.$$

The equilibrium vector is

$$\alpha^*=X_0=\begin{pmatrix}0.1000\\0.2000\\0.4000\\0.2000\end{pmatrix}.$$

We now calculate

$$X_1=\alpha_{x_1}(0)-X_0=\begin{pmatrix}0.2214\\-0.3000\\-0.3618\\0.4404\end{pmatrix}.$$

In order to select a new composition, we use the following procedure. We calculate the vectors $\bar{X}_0$ and $\bar{X}_1$ in the coordinate system B:

$$\bar{X}_0=D^{-1/2}X_0=\begin{pmatrix}0.316228\\0.547723\\0.632456\\0.447214\end{pmatrix}.$$

After similar calculations and normalisation, we obtain

$$\bar{X}_1=\begin{pmatrix}0.484615\\-0.379123\\-0.395966\\0.681634\end{pmatrix}.$$

We now contruct a vector orthogonal with respect to X_1 and X_0 and use it to calculate the initial composition. We set up the vector

$$\bar{\gamma}_1=\begin{pmatrix}0.0000\\-0.622456\\0.547723\\0.000000\end{pmatrix}.$$

Evidently γ_1 is orthogonal with respect to $\bar{X}_1$. We calculate

$$\bar{\gamma}_2=\bar{\gamma}_1-(\bar{X}_1,\bar{\gamma}_1)=\begin{pmatrix}-0.011097\\-0.623774\\0.556790\\-0.015609\end{pmatrix}.$$

After the transformation of γ_2 so that it applies to a non-orthogonal coordinate system and a change in length, we obtain

$$X_{2'}=\begin{pmatrix}-0.003081\\-0.30000\\0.309211\\-0.006130\end{pmatrix},$$

$$\alpha(0)=X_{2'}+X_0=\begin{pmatrix}0.0969\\0.0000\\0.7092\\0.1939\end{pmatrix}.$$

After repeating the successive approximations, starting from this composition, we obtain the vector

$$X_2=\begin{pmatrix}-0.011748\\-0.300000\\0.309178\\0.002571\end{pmatrix}.$$

The vector X_3 may be calculated from the orthogonality relations. Further calculations differed in insignificant details only from the case of a three-dimensional system examined above.

The isomerisation reactions of xylenes have been investigated[24] by a similar method. The experimental linear reaction pathways have been used[25] to test the calculated rate constants.

H. The Structure of Systems of First-Order Reversible Reactions

We shall now summarise the discussion of systems of unimolecular reversible reactions. The structure of these systems is fully described by the theorems formulated above. We found that there are n characteristic vectors with non-positive eigenvalues for reversible reactions in an n-dimensional composition space. Any solution of Eqns. (3) (or the reaction pathway) is a linear combination of characteristic vectors with time-dependent coefficients. One of the characteristic vectors, with a zero eigenvalue, is a positively defined equilibrium vector. The remaining characteristic vectors contain negative elements. However, a linear combination of each non-equilibrium characteristic vector with the equilibrium vector yields a non-negatively defined vector. Therefore all non-equilibrium characteristic vectors are quasipositive. A linear reaction pathway located in the positive octant of the vector space corresponds to any quasipositive vector. All these linear pathways can be observed experimentally. The determination of $n - 1$ linear reaction pathways makes it possible to calculate the matrix of relative rate constants without measuring the reaction time. The system of reversible unimolecular reactions approaches the unique equilibrium point monotonically, oscillations in the system being impossible. Curved reaction pathways approaching the equilibrium point via a spiral curve are therefore also impossible.

3. FIRST-ORDER SYSTEMS INVOLVING REVERSIBLE AND IRREVERSIBLE REACTIONS

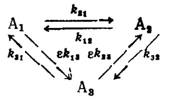
A. The Form of the Kinetic Matrix

The structure of systems containing irreversible steps is significantly more complex than the structure of reversible reactions examined above. This is associated primarily with the fact that the principle of detailed balancing does not hold for systems involving irreversible steps. On the basis of this principle, we showed above that there is a complete system of characteristic vectors for reversible reactions in an n-dimensional composition space and also that the positive octant of the vector space contains $n - 1$ linear reaction pathways. The study of these pathways actually made it possible to devise a method for the determination of the rate constants. A system of reversible reactions approaches the unique equilibrium point regardless of the chosen initial composition. When irreversible steps are present in the system, there may be an infinite number of equilibrium points, there may not be a complete system of characteristic vectors, and the linear reaction pathways may originate from the positive octant of the vector space. The study of irreversible reactions therefore requires a new approach, which will now be discussed.

We shall consider irreversible steps as the limiting cases of reversible stages, involving large changes in free energy or a large decrease in the corresponding rate constants[26]. For example, the simple scheme

(IV)

can be regarded as the limiting case of the scheme



(V)

when $\epsilon \rightarrow 0$. We shall show what information can be derived from the principle of detailed balancing in such a limiting transition. The Wegsheider condition for scheme (V) yields $k_{12}k_{23}k_{31} = k_{32}k_{21}k_{13}$. The rate constant matrix for scheme (V)

$$\begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & \varepsilon k_{13} \\ k_{21} & -(k_{12}+k_{32}) & \varepsilon k_{23} \\ k_{31} & k_{32} & -\varepsilon(k_{13}+k_{23}) \end{pmatrix}$$

becomes the kinetic matrix for system (IV) when $\epsilon \rightarrow 0$:

$$\begin{pmatrix} -(k_{21}+k_{31}) & k_{12} & 0 \\ k_{21} & -(k_{12}+k_{32}) & 0 \\ k_{31} & k_{32} & 0 \end{pmatrix} . \qquad (41)$$

The equilibrium concentrations for scheme (V) are calculated from the principle of detailed balancing:

$$\begin{aligned} a_1^{*} &= \varepsilon\,(k_{13}/k_{31})\,a_3^{*}, \\ a_2^{*} &= \varepsilon\,(k_{23}/k_{32})\,a_3^{*}, \\ a_3^{*} &= a_3^{*}. \end{aligned} \qquad (42)$$

The equilibrium composition matrix D changes in the following way when $\epsilon \rightarrow 0$:

$$\begin{pmatrix} a_1^{*} & 0 & 0 \\ 0 & a_2^{*} & 0 \\ 0 & 0 & a_3^{*} \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The matrix D for scheme (IV) is degenerate, so that $D^{-1/2}$ does not exist and reduction to the symmetrical form which we used above is no longer possible. However, it follows from the principle of detailed balance that the ratio of the equilibrium concentrations is independent of ϵ:

$$\frac{a_1^{*}}{a_2^{*}} = \frac{k_{13}k_{23}}{k_{31}k_{32}} = \frac{k_{12}}{k_{21}}. \qquad (43)$$

It follows from Eqn. (43) that

$$\frac{a_1^{*}}{a_1^{*}+a_2^{*}} = \frac{k_{12}}{k_{12}+k_{21}}; \quad \frac{a_2^{*}}{a_1^{*}+a_2^{*}} = \frac{k_{21}}{k_{12}+k_{21}}.$$

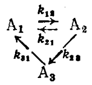
We now construct the matrix

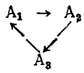
$$D = \begin{pmatrix} \dfrac{k_{12}}{k_{12}+k_{21}} & 0 & 0 \\ 0 & \dfrac{k_{21}}{k_{12}+k_{21}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (44)$$

and calculate

$$D^{-1/2}KD^{1/2} = \begin{pmatrix} \begin{bmatrix} -(k_{21}+k_{31}) & (k_{12}k_{21})^{1/2} \\ (k_{12}k_{21})^{1/2} & -(k_{12}+k_{23}) \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} k_{13} & \qquad k_{32} \end{matrix} & 0 \end{pmatrix}. \qquad (45)$$

Evidently the submatrix enclosed in brackets is symmetrical. Thus, using the limiting form of the principle of detailed balancing, it is possible to reduce to a symmetrical form the submatrices corresponding to subsystems with reversible reactions. We shall use this fact below for the description of complex systems involving irreversible steps. However, one should note here that we shall be forced to restrict somewhat the range of subsystems considered. We shall postpone until the next section the study of systems involving cycles of irreversible reactions. For example, schemes of the type

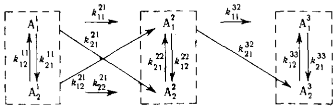

(VI)


(VII)

are not analysed, because they cannot be regarded as limiting cases of the corresponding schemes for reversible reactions, since the Wegsheider condition is infringed in the limiting transition, i.e. the principle of detailed balance ceases to hold. In fact, we shall attempt to represent scheme (VI) as the limiting case of scheme (V) when the constants k_{32} and k_{13} tend to zero. Both these constants enter into the right-hand side of Eqn. (12), so that the condition defined by this equation breaks down when k_{32} and k_{13} decrease.

Below we shall formulate rigorously the class of systems to be considered. To extend the treatment from an example to the general case, we shall introduce certain concepts and symbols.

The irreversible stages in the general system can be isolated by subdividing the system into reversible subsystems linked by irreversible stages. We shall combine substances linked by reversible reactions into subsystems and shall consider the reactions between these subsystems, assuming them to be identical with fictitious simple substances. We shall consider the following scheme:



(VIII)

This system can be divided into subsystems:

$$M^1 \leftrightarrow \overset{A_1^1}{\underset{A_2^1}{\downarrow\uparrow}}\ ;\ M^2 \leftrightarrow \overset{A_1^2}{\underset{A_2^2}{\downarrow\uparrow}}\ ;\ M^3 \leftrightarrow \overset{A_1^3}{\underset{A_2^3}{\downarrow\uparrow}}\quad . \tag{IX}$$

The entire system can then be represented thus: $M^1 \rightarrow M^2 \rightarrow M^3$. In designating the substances, the superscript refers to the number of the subsystem and the subscript to the number of the substance in the subsystem. The kinetic matrix assumes the following form:

$$K=\begin{pmatrix} \begin{bmatrix} -(k_{21}^{11}+k_{11}^{21}+k_{21}^{21}) & k_{12}^{11} \\ k_{21}^{11} & -(k_{12}^{11}+k_{12}^{21}+k_{22}^{21}) \end{bmatrix} & \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \\ \begin{bmatrix} k_{11}^{21} & k_{12}^{21} \\ k_{21}^{21} & k_{22}^{21} \end{bmatrix} & \begin{bmatrix} -(k_{11}^{22}+k_{11}^{32}+k_{21}^{32}) & k_{12}^{22} \\ k_{21}^{22} & -k_{12}^{22} \end{bmatrix} & \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \\ \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} & \begin{bmatrix} k_{11}^{32} & 0 \\ k_{21}^{32} & 0 \end{bmatrix} & \begin{bmatrix} -k_{21}^{33} & k_{12}^{33} \\ k_{21}^{33} & -k_{12}^{33} \end{bmatrix} \end{pmatrix}.$$

In designating the rate constants, the superscripts again refer to the numbers of the subsystems and the subscripts to the numbers of the substances. The first subscript refers to the reaction product and the second to the starting material. Thus the rate constant for the reaction $A_5^1 \rightarrow A_4^3$ is designated by k_{45}^{31}.

If the submatrices enclosed in square brackets are designated by K^{ij}, we find that

$$K=\begin{pmatrix} K^{11} & 0 & 0 \\ K^{21} & K^{22} & 0 \\ 0 & K^{32} & K^{33} \end{pmatrix}. \tag{46}$$

Evidently the kinetic matrix in the example considered is triangular.

We shall now deal with the general case. We shall put $M^\alpha \rightarrow M^\beta$ only when there is a series of consecutive reactions leading from subsystem M^α to subsystem M^β. For example $M^\alpha \rightarrow M^\beta$ if the following sequence of reactions occurs:

$$M^\alpha \rightarrow M^{\alpha+1} \rightarrow M^\beta \quad . \tag{X}$$

We shall consider systems in which there are only three possibilities: (1) $M^\alpha \rightarrow M^\beta$; (2) $M^\beta \rightarrow M^\alpha$; (3) there is no interaction between M^α and M^β. Conditions 1 and 2 cannot be fulfilled simultaneously. It is readily seen that cycles are thus excluded from consideration. Conditions 1–3 determine the form of the kinetic matrix. We shall assign to the subsystems superscripts such that $\beta > \alpha M^\alpha \not\rightarrow M^\beta$, i.e. all the rate constants for the conversion of A_i^β into A_i^α are zero. After the introduction of such numbering of the subsystems, it is possible to formulate the kinetic matrix as follows:

$$K=\begin{pmatrix} K^{11} & \dots\dots\dots & \\ K^{21} & K^{22} & \dots\dots \\ \dots & \dots\dots & \dots \\ K^{\nu 1} & \dots\dots & K^{\nu\nu} \end{pmatrix}, \tag{47}$$

where the submatrices $K^{\beta\alpha}$ are the matrices of the rate constants for the irreversible reactions leading from M^α to M^β.

The diagonal submatrices $K^{\alpha\alpha}$ can be written as follows:

$$K^{\alpha\alpha}=K^{m\alpha}+\Sigma^{\cdot\alpha}, \tag{48}$$

where $\Sigma^{\cdot\alpha}$ is the diagonal matrix corresponding to the irreversible reactions leading from M^α. The diagonal elements of $\Sigma^{\cdot\alpha}$ are equal to the sum of the elements of the corresponding column with the sign reversed. Systems with a kinetic matrix of type (47) are considered below.

B. The Eigenvalues

We shall set up for each diagonal submatrix a matrix of equilibrium ratios D^α, as was done in the example analysed above. We define for the entire system a non-degenerate diagonal matrix $D^{1/2}$:

$$D^{1/2}=\begin{pmatrix} (D^1)^{1/2} & & & \\ & (D^2)^{1/2} & & \\ & & \ddots & \\ & & & (D^\nu)^{1/2} \end{pmatrix}, \tag{49}$$

where $(D^i)^{1/2}$ is the matrix of the equilibrium ratios for the irreversible subsystem M^i. The element with the number jj in the matrix $(D^i)^{1/2}$ is

$$[(a_j^i)^*]^{1/2}/\left[\sum_i (a_i)^*\right]^{1/2}.$$

It can be shown that the diagonal submatrices $B^{\alpha\alpha}$ of the matrix $B = D^{-1/2}KD^{1/2}$ are symmetrical. Hence follows theorem 3: The diagonal submatrices $K^{\alpha\alpha}$ of the triangular kinetic matrix K for a system involving reversible and irreversible stages possess a complete system of characteristic vectors.

It has also been shown[26] that the matrix of the characteristic vectors for the kinetic matrix K is triangular:

$$X=\begin{pmatrix} X^{11} & 0 & \dots\dots & 0 \\ X^{21} & X^{22} & \dots\dots & 0 \\ \dots & \dots & \dots\dots & \dots \\ X^{\nu 1} & \dots & \dots\dots & X^{\nu\nu} \end{pmatrix}, \tag{50}$$

where $X^{\alpha\beta}$ is the matrix of the characteristic vectors of the submatrix $K^{\alpha\beta}$. There are m relations of the type

$$K^{\alpha\alpha}X^{\alpha\alpha}=X^{\alpha\alpha}\Lambda^\alpha, \tag{51}$$

where m is the total number of reversible subsystems and Λ^{α} the matrix of the eigenvalues of the submatrix $K^{\alpha\alpha}$.

We therefore have theorem 4: all the eigenvalues of the kinetic matrix K are fully defined by the submatrices $K^{\alpha\alpha}$.

Corollary 1. All the eigenvalues of the matrix K are non-positive.

Corollary 2. Oscillations are impossible in a system involving reversible and irreversible first-order reactions with a triangular matrix K.

We found that each diagonal submatrix $K^{\alpha\alpha}$ has a complete system of characteristic vectors. However, from this it does not yet follow that the entire matrix K is a complete system of characteristic vectors. This is true only when the eigenvalues of the submatrices $K^{\alpha\alpha}$ and $K^{\beta\beta}$ are not the same. When the eigenvalues are the same, cases are possible where the kinetic matrix cannot be reduced to the diagonal form. Nevertheless, in practice the matrix K should usually have a complete system of eigenvectors. We shall prove the validity of this case and shall discuss it below.

C. Disposition of the Characteristic Vectors

We recall that a linear reaction pathway in the composition space corresponds to each characteristic vector. We are interested only in the linear pathways located in the positive octant of the space. For a system of reversible reactions, the non-equilibrium vectors were found to be quasipositive and the corresponding linear reaction pathways could be observed experimentally. We shall attempt to elucidate the disposition of the characteristic vectors in a system involving reversible and irreversible stages.

Definition 4. The subsystem M^{ν} is called finite if there are no irreversible reactions leading from this subsystem to others. A system may contain several finite subsystems. For example the subsystems M_5 and M_4 in the scheme

$$\begin{tikzcd} M_1 \arrow[r] \arrow[d] & M_2 \arrow[r] & M_3 \arrow[dl] \\ M_5 & M_4 & \end{tikzcd} \qquad \text{(XI)}$$

are finite.

In each of s finite closed subsystems, there is an equilibrium positively defined characteristic vector $X_e^{\nu\nu}$. Thus the entire system contains s characteristic vectors of the type

$$X_e^{\nu} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ X_e^{\nu\nu} \end{pmatrix}, \qquad (52)$$

where X_e^{ν} is a column vector of the matrix X. All the linear combinations of these vectors are the equilibrium points of the system involving irreversible stages and all the equilibrium points are linear combinations of the equilibrium vectors. Thus the system contains s independent positive vectors in the positive octant.

A linear combination of equilibrium and non-equilibrium characteristic vectors in the systems considered does not necessarily give rise to a positively defined vector, since the equilibrium point is located in the composition subspace. In fact a criterion for the existence of quasipositive vectors, arising from the open subsystem $M^{\alpha}\rightarrow$, readily follows from the equation for a system with a unique equilibrium point:

$$\alpha_{x_i} = X_i^{\alpha} + X_e^{\nu} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ X_i^{\alpha\alpha} \\ X_i^{\alpha+1,\alpha} \\ \vdots \\ X_i^{\nu\alpha} \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ X_e^{\nu\nu} \end{pmatrix}. \qquad (53)$$

Theorem 5. For the characteristic vector X_i^{α}, where $\alpha < \nu$, to be quasipositive, it is necessary and sufficient that all the subvectors $X_i^{\beta\alpha}$ should contain only non-negative elements.

Theorem 6[26]: The matrix $X^{\alpha\alpha}$ for the open subsystem $M^{\alpha}\rightarrow$ contains one and only one subvector $X_i^{\alpha\alpha}$, all the elements of which are non-negative. The existence of the positively defined vector follows from Wei's theorem[27], namely theorm 7: one of the following statements is valid for a system of first-order reactions including any number of components: either the equilibrium composition is non-zero or there is at least one linear pathway in the positive octant of the space.

Hence follows the conclusion that, which the system contains u open subsystems of type $M^{\alpha}\rightarrow$, there are at most u quasipositive vectors arising from these subsystems.

We shall consider yet another special case of subsystems such that there are no reactions leading from them to other open subsystems and there are only reactions leading to a finite subsystem. Subsystems of this kind are called adjacent to the finite system. Since the characteristic vector X_i^{α} for such a subsystem does not contain the subvectors $X_i^{\beta\alpha}$, where β is an open subsystem, it follows that there is always one quasipositive vector for each subsystem adjoining the finite system. If the system contains v adjacent subsystems, one can assert that there are v quasipositive vectors.

We shall also consider a pair of transitional subsystems of the type

$$\begin{tikzcd} M^{\alpha} \arrow[r] \arrow[d] & M^{\beta} \arrow[d] \\ {} & {} \end{tikzcd} . \qquad \text{(XII)}$$

It is of interest to obtain a criterion of the absence of negative elements from the subvectors $X_r^{\beta\alpha}$.

This criterion is given by therem 8: for transitional subsystems (XII), the subvector $X_r^{\beta\alpha}$, where M^{β} is an intermediate subsystem (not adjacent to the finite system) will not contain negative elements when $|\lambda_r^{\alpha}| < |\lambda_r^{\beta}|$ and will contain non-positive elements when $|\lambda_r^{\alpha}| > |\lambda_r^{\beta}|$.

We can now summarise the findings obtained from the consideration of the structure of systems involving irreversible stages. A complex system with reversible and irreversible stages can be conveniently represented by reversible subsystems linked by irreversible stages. It is possible to isolate two principal differences from systems involving reversible reactions only. The first is that the matrix K cannot always be reduced to a diagonal form. However, in practice such instances should not arise frequently. It is therefore more important that not all the characteristic vectors are quasipositive and the corresponding linear pathways cannot be observed experimentally. The following statements may be made about the disposition of the eigenvectors:

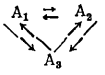
1. There exists a positively defined equilibrium characteristic vector for each finite subsystem.
2. All non-equilibrium characteristic vectors, arising from a finite subsystem, are quasipositive. The corresponding linear pathways can be observed experimentally.
3. The number q of quasipositive vectors arising from intermediate subsystems is between u (the number of all intermediate subsystems) and v (the number of subsystems adjoining the finite system).

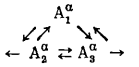
Thus the characteristic vectors for systems involving irreversible stages are frequently not located in the positive quadrant of the composition space and it is impossible to obtain the positive vector from a linear combination of equilibrium and non-equilibrium characteristic vectors. A "projection" method has therefore been proposed[28] whereby artificial linear reaction pathways may be obtained.

D. Artificial Linear Reaction Pathways. Projection Method

The essential feature of the method in the simplest case reduces to the consideration, instead of the open subsystem $M^{\alpha}\rightarrow$, of a closed subsystem $\hat{M}^{\alpha}$, which is obtained by adding to the subsystem the mass loss as a result of irreversible reactions away from the subsystem. Geometrically this implies the projection of the reaction pathways on the (1, 1, ..., 1) hyperplane.

Projection of the principal subvectors $X^{\alpha\alpha}$. We shall compare initially a reversible closed system M with a subsystem $M^{\alpha}\rightarrow$ in relation to three-component systems:


(XIII)


(XIV) .

In each of these systems, there is a positively defined characteristic vector. In the first case, this is an equilibrium vector X_e and in the second a vector $X_r^{\alpha\alpha}$. The equilibrium vector X_e contains the entire mass of the system M and the sum of all the elements of non-equilibrium characteristic vectors is zero. In other words, all the characteristic vectors X_i with $i \neq e$ are perpendicular to the unit vector I (1, ..., 1) and they are therefore located in the (1, 1, ..., 1) hyperplane. On the other hand, the $X_r^{\alpha\alpha}$ does not contain the mass of the entire system and the vectors $X_r^{\alpha\alpha}$ and I may not in fact be perpendicular. The disposition of the characteristic vectors is illustrated in Figs. 8 and 9. When the initial vector $a_x(0)$ of a closed system M is located in the plane of the equilibrium vector and one of the non-equilibrium characteristic vectors, the movement of the system towards equilibrium is given by the equation

$$a_x(t)=X_e+b_i(t)X_i. \tag{54}$$

Thus a natural linear reaction pathway in the (1, 1, ..., 1) hyperplane arises for each characteristic vector X_i. All the curved reaction pathways are also located in the (1, 1, ..., 1) hyperplane. For the system $M^{\alpha}\rightarrow$, the reaction pathways can no longer be located in the plane perpendicular to the vector I, since the equilibrium point which the system approaches coincides with the origin of coordinates. If the initial vector is located in the plane of the vector $X_r^{\alpha\alpha}$ and one of the other characteristic vectors $X_i^{\alpha\alpha}$, then the movement towards equilibrium can be described by the equation

$$a_x(t)=b_r^{\alpha}X_r^{\alpha\alpha}+b_i^{\alpha}(t)X_i^{\alpha\alpha}. \tag{55}$$

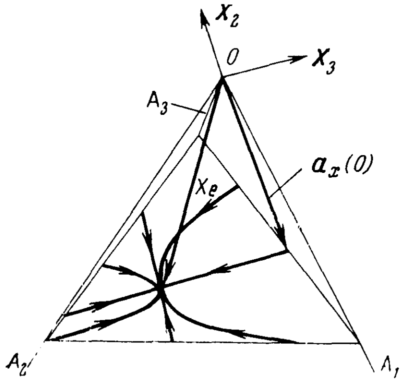


Figure 8. Reaction pathways and characteristic vectors for the system (XIII).

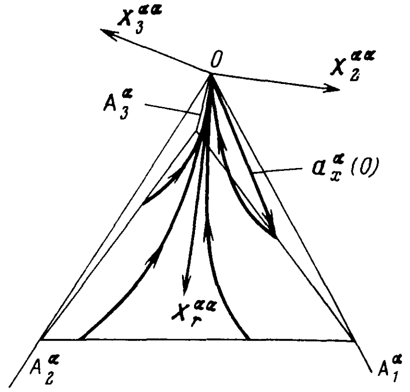


Figure 9. Reaction pathways and characteristic vectors for the system (XIV).

Since the vectors $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$ are non-zero, we obtain a curved reaction pathway. The only linear reaction pathway located in the positive octant of the vector space therefore coincides with the direction of the vector $X_r^{\alpha\alpha}$. Furthermore, Eqn. (55) shows that any composition vector located in the plane of $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$ for $t = 0$ remains in this plane subsequently. Thus the reaction pathway for the system $M^{\alpha}\rightarrow$ consists in the general case of a spatial curve. If this curve is projected onto the

(1, 1, ..., 1) hyperplane, it is possible to obtain an artificial linear reaction pathway. Fig. 10 illustrates a projection parallel to the vector $X_r^{\alpha\alpha}$, which yields an artificial linear reaction pathway.

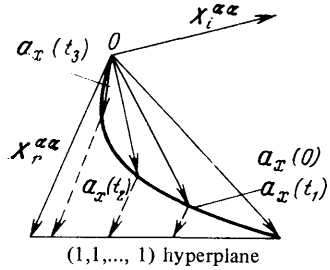
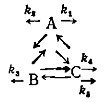


Figure 10. Projection of curved reaction pathways on the (1, 1, ..., 1) hyperplane.

We shall consider initially the specific case of the subsystems $M^\alpha \rightarrow$, where the sum of the rate constants for the irreversible reactions involving the ith substance of the subsystem is independent of the number i. Thus, for the subsystem



(XV)

this implies that $k_1 + k_2 = k_3 = k_4 + k_5 = c =$ const. When the length of the characteristic vectors is chosen suitably, the following expression can be formulated for the reaction pathway in the subsystems considered:

$$a^\alpha(t) = e^{-ct} X_r^{\alpha\alpha} + \sum_{l=2}^{n^\alpha} b_l(t) X_l^{\alpha\alpha}, \tag{56}$$

where n^α is the dimension of the subsystem $M^\alpha \rightarrow$. The entire mass of the system is concentrated at $X_r^{\alpha\alpha}$ and the remaining characteristic vectors are perpendicular to the unit vector I = (1, 1, ..., 1). The loss of mass from the system owing to irreversible reactions is $X_r^{\alpha\alpha} - e^{-ct} X_r^{\alpha\alpha}$. Projection parallel to the direction of the vector $X_r^{\alpha\alpha}$ is equivalent to an artificial compensation for the mass lost as a result of the irreversible reactions. The artificial composition vector $\hat{a}^\alpha(t)$, arising on projection, is defined by the equation

$$\hat{a}^\alpha(t) = X_r^{\alpha\alpha} + \sum_{l=2}^{n^\alpha} b_l(t) X_l^{\alpha\alpha}. \tag{57}$$

We obtained an equation for a closed system of reversible reactions with an artificial equilibrium point $X_r^{\alpha\alpha}$.

We shall now consider the general case of subsystems $M^\alpha \rightarrow$. In the general case, it is no longer possible to assume that all the vectors $X_i^{\alpha\alpha}$ are orthogonal with respect to the unit vector I (1, 1, ..., 1). The following equation holds for the reaction pathway:

$$a^\alpha(t) = b_r^\alpha(t) X_r^{\alpha\alpha} + \sum_k b_k^\alpha(t) X_k^{\alpha\alpha} + \sum_j b_j^\alpha(t) X_j^{\alpha\alpha}, \tag{58}$$

where the vectors $X_k^{\alpha\alpha}$ are orthogonal with respect to the unit vector I, a condition which does not hold for the $X_j^{\alpha\alpha}$. The number of vectors $X_k^{\alpha\alpha}$ and $X_j^{\alpha\alpha}$ is unimportant and the only significant factor is that the total number of characteristic vectors $X_i^{\alpha\alpha}$ (for $i \neq r$) is equal to $n^\alpha - 1$. The length of the characteristic vectors orthogonal with respect to I will be chosen so that the vectors are located in the (1, 1, ..., 1) hyperplane.

We showed above that, when $M^\alpha \rightarrow$ is projected, it is converted into a closed subsystem $\hat{M}^\alpha$ with an equilibrium point $X_r^{\alpha\alpha}$. Since $X_r^{\alpha\alpha}$ contains the entire mass in the transformed subsystem $\hat{M}^\alpha$, the remaining characteristic vectors must be orthogonal to the unit vector I. Eqn. (58) can therefore be transformed in such a way that all the vectors other than $X_r^{\alpha\alpha}$ are orthogonal to the unit vector. Since the vectors $X_r^{\alpha\alpha}$ and $X_j^{\alpha\alpha}$ are located in the (1, 1, ..., 1) hyperplane, the vector $X_r^{\alpha\alpha} - X_r^{\alpha\alpha}$ must be located in a plane parallel to this hyperplane. The required transformation can therefore be obtained by adding $\Sigma b_i(t) X_r^{\alpha\alpha}$ to the first term of Eqn. (58) and by substracting it from the last term:

$$a^\alpha(t) = \left\{ b_r(t) + \sum_j b_j(t) \right\} X_r^{\alpha\alpha} + \sum_k b_k^\alpha(t) X_k^{\alpha\alpha} + \sum_j b_j^\alpha(t) (X_j^{\alpha\alpha} - X_r^{\alpha\alpha}). \tag{59}$$

We shall now consider an artificial system $\hat{M}^\alpha \rightarrow$ obtained by projecting the vector $a^\alpha(t)$ onto the (1, 1, ..., 1) hyperplane parallel to $X_r^{\alpha\alpha}$. The weight loss from the system is

$$\left[b_r^\alpha(0) + \sum_j b_j^\alpha(0) \right] X_r^{\alpha\alpha} - \left[b_r^\alpha(t) + \sum_j b_j^\alpha(t) \right] X_r^{\alpha\alpha}. \tag{60}$$

In order to obtain the artificial system, we add this amount to $a^\alpha(t)$ defined by the Eqn. (59):

$$\hat{a}^\alpha(t) = X_r^{\alpha\alpha} + \sum_k b_k^\alpha(t) X_k^{\alpha\alpha} + \sum_j b_j^\alpha(t) (X_j^{\alpha\alpha} - X_r^{\alpha\alpha}). \tag{61}$$

The last equation is valid for an artificial closed system of reversible first-order reactions with a matrix $\hat{K}_{\alpha\alpha}$. The eigenvector matrix for $\hat{K}_{\alpha\alpha}$ is

$$\hat{X}^{\alpha\alpha} = (X_r^{\alpha\alpha}, \ldots\ldots X_k^{\alpha\alpha} \ldots\ldots (X_j^{\alpha\alpha} - X_r^{\alpha\alpha})). \tag{62}$$

Projection in non-diagonal subsystems. In the previous section we considered the principal systems whose kinetic matrices are located on the diagonal of the matrix for the entire system. We shall now consider non-diagonal transitional subsystems.

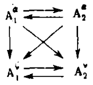
We shall analyse initially two special cases: the system

$$M^\alpha \rightarrow M^\nu \quad , \tag{XVI}$$

where M^ν is a finite subsystem and

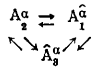
$$\underset{\downarrow}{M^\alpha} \rightarrow \underset{\downarrow}{M^\beta} \text{ when } K^{\beta\alpha} \neq 0 \ . \tag{XVII}$$

The system (XVI) is closed and all the characteristic vectors, except the equilibrium vector X_e^ν, are perpendicular to the vector I. The equilibrium vector X_e^ν is of the form $X_e^\nu = \begin{pmatrix} 0 \\ X_e^{\nu\nu} \end{pmatrix}$. The only quasipositive characteristic vector will be designated by X_e^α. The possibility of obtaining artificial reaction pathways by projection will be examined in relation to the system



(XVIII)

Fig. 11 illustrates the (1, 1, 1, 1) hyperplane for the system (XVIII). The natural linear reaction pathway X_2^α is not located in the positive octant of the vector space. The curved reaction pathway, beginning in the (X_r^α, X_i^α) plane, remains in this plane until the attainment of the equilibrium point X_e^α. By projecting the curved pathway onto the subspace (1, 1, 0, 1), one can therefore obtain an artificial linear pathway in a finite segment of the positive octant. Such projection converts the system (XVIII) into the artificial system



(XIX)

The artificial equilibrium point N for the system (XIX) coincides with the point of intersection of the line of the vector X_r^α with subspace (1, 1, 0, 1).

Returning now to the general case, the equation for the system $M^\alpha \rightarrow M^\nu$ will be written in the form

$$a(t) = X_e^\nu + b_r^\alpha(t)X_r^\alpha + \sum_{i=2}^{n^\nu} b_i^0(t)X_i^\nu + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)X_i^\alpha. \tag{63}$$

We transform Eqn. (63) into the equation for a system of reversible reactions from which the component A_j^ν has been excluded. The final result is

$$\hat{a}(t) = \{X_e^\nu + CX_r^\alpha\} + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)\{X_i^\alpha - \varphi_i^\alpha X_r^\alpha\} + \sum_{i=2}^{n^\nu} b_i^\nu(t)\{X_i^\nu - \varphi_i^\nu X_r^\alpha\}, \tag{64}$$

where the scalars φ_i^k ($k = \alpha$ or ν) have been chosen so that $(X_{ik} - \varphi_i^k X_{jr}) = 0$; the constant C is chosen so that

$$\hat{a}_j^\nu = X_{je}^{\nu\nu} + CX_{jr}^{\nu\alpha} = 0. \tag{65}$$

The initial composition for the artificial linear pathway is determined from the equation

$$\hat{a}(0) = \{X_e^\nu + CX_r^\alpha\} + b_i^k(0)\{X_i^k - \varphi_i^k X_r^\alpha\}, \tag{66}$$

where $k = \alpha$ or ν.

It must be emphasised that a natural linear reaction pathway is a simple linear combination of the equilibrium vector and one non-equilibrium characteristic vector. On the other hand, an artificial linear pathway is a linear combination of several characteristic vectors,

We shall now consider the open system (XVII). We shall ignore all stages after $M^\alpha \rightarrow$ and $M^\beta \rightarrow$ and shall take into account only the subspace corresponding to $M^\alpha \rightarrow$ and $M^\beta \rightarrow$. The subvectors

$$X_i^u = \begin{pmatrix} X_i^{\alpha\alpha} \\ X_i^{\beta\alpha} \end{pmatrix}, \quad X_i^\beta = \begin{pmatrix} 0 \\ X_i^{\beta\beta} \end{pmatrix} \tag{67}$$

are the characteristic vectors of the subsystem (XVII).

We shall consider two cases of interest. It was shown previously that, when $\lambda_r^\alpha < \lambda_r^\beta$, then X_r^u should be a non-negative vector. It is possible to show that X_r^u consists of positive elements only. For the scheme (XVII), one can write the following equation:

$$a^u(t) = b_r^\alpha(t) + b_r^\beta(t)X_r^\beta + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)X_i^u + \sum_{i=2}^{n^\beta} b_i^\beta(t)X_i^\beta. \tag{68}$$

We shall assume, to make the treatment concrete, that none of the characteristic vectors is perpendicular to the vector I. Furthermore, the length of the characteristic vectors is chosen so that they are located in the (1,1,...,1) hyperplane.

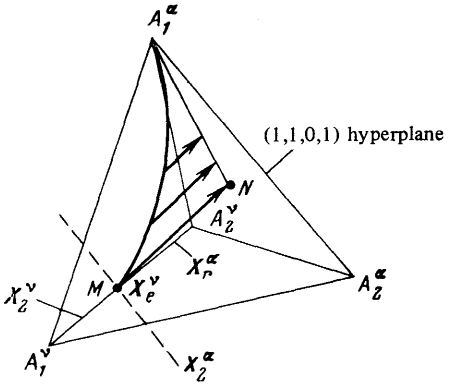


Figure 11. Parallel projection for the system (XVIII); M—equilibrium point; N—artificial equilibrium point.

Eqn. (68) can then be rewritten in the form

$$\begin{aligned} a^u(t) = {} & (b_r^\alpha(t) + b_r^\beta(t)) + \sum_{i=2}^{n^\alpha} b_i^\alpha(t) + \sum_{i=2}^{n^\beta} b_i^\beta(t)X_r^u + \\ & + b_r^\beta(t)\{X_r^\beta - X_i^u\} + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)(X_i^u - X_r^u) + \sum_{i=2}^{n^\beta} b_i^\beta(t)(X_i^\beta - X_r^u). \end{aligned} \tag{69}$$

In Eqn. (69) the vectors $X_j^R - X_r^u$ ($j = i$ or r, $R = u$ or β) are perpendicular to the vector I. The entire loss of mass takes place along X_r^u. Parallel projection results in compensation for the loss of mass from the system:

$$\hat{a}^u(t) = X^u + b_r^\beta(t)\{X_r^\beta - X_i^u\} + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)\{X_i^u - X_r^u\} + \sum_{i=2}^{n^\beta} b_i^\beta(t)(X_i^\beta - X_r^u). \tag{70}$$

Eqn. (70) is the equation for a closed system of reversible reactions with an artificial equilibrium point X_r^u. The initial compositions for artificial linear reaction pathways are

$$\begin{aligned} \hat{a}_x(0) &= X_r^u + b_i^\alpha(0)(X_i^u - X_r^u), \ i \neq r; \\ \hat{a}_x(0) &= X_r^u + b_i^\beta(0)(X_i^\beta - X_r^u). \end{aligned} \tag{71}$$

We shall now consider the case where $\lambda_r^\alpha > \lambda_r^\beta$. The subvector $X_r^{\beta\alpha}$ must contain negative elements and X_r^u is not located in the positive octant. In this case, the vector X_r^u can be used to transform the open system (XVII) into a closed system. By carrying out transformations similar to those described above, we obtain

$$\begin{aligned} \hat{a}^u(t) = {} & X_r^\beta + b_r^\alpha(t)\{X_r^u - X_r^\beta\} + \\ & + \sum_{i=2}^{n^\alpha} b_i^\alpha(t)\{X_i^u - X_r^\beta\} + \sum_{i=2}^{n^\beta} b_i^\beta(t)\{X_i^\beta - X_r^\beta\}. \end{aligned} \tag{72}$$

The initial composition for a linear reaction pathway is determined from

$$\hat{a}_x(0)=X_r^{\beta}+b_i^{\alpha}(0)\{X_i^{u}-X_r^{\beta}\}. \tag{73}$$

Since $X_r^{\beta} = \begin{pmatrix}0\\ X_i^{\beta\beta}\end{pmatrix}$ and X_i^{u} contains negative elements for $i \neq r$, a linear pathway located in the positive octant is obtained only when the vector X_r^{β} is used. Next, suppose that $i \neq r$. Eqn. (72) can be regarded as one describing an artificial closed system $\hat{M}^{\alpha} \rightarrow \hat{M}^{\beta}$. Using a method similar to that described above, this system can be transformed into a system of reversible reactions with the exclusion of one component. The final result is

$$\begin{aligned}\hat{\hat{a}}^{u}(t)=X_r^{\beta}+C(X_r^{u}-X_r^{\beta})+\sum_{i=1}^{n^{\alpha}} b_i^{\alpha}(t)\{X_i^{u}-X_r^{\beta}-\varphi_i^{u}(X_r^{u}-X_r^{\beta})\}+\\ +\sum_{i=1}^{n^{\beta}} b_i^{\beta}(t)\{X_i^{\beta}-X_r^{\beta}-\varphi_i^{\beta}(X_r^{u}-X_r^{\beta})\}.\end{aligned} \tag{74}$$

The initial composition for a linear pathway is given by the formula

$$\hat{\hat{a}}_x(0)=X_r^{u}+C(X_r^{u}-X_r^{\beta})+b_i^{\alpha}(0)\{X_i^{u}-X_r^{\beta}-\varphi_i^{u}(X_r^{u}-X_r^{\beta})\}. \tag{75}$$

We shall now show how these results can be used to determine the rate constants.

E. Definition of the Rate Constants

Rate Constants for Reversible Reactions. All the constants for reversible reactions are located in the diagonal submatrices $K^{\alpha\alpha}$. It was shown above that

$$K^{\alpha\alpha}=X^{\alpha\alpha}\Lambda^{\alpha}(X^{\alpha\alpha})^{-1}. \tag{76}$$

If the principal subvectors $X_i^{\alpha\alpha}$ have been found, it is possible to determine the eigenvalues λ^{α}. Then, knowing $X_i^{\alpha\alpha}$ and the matrix Λ^{α}, it is possible to calculate the rate constant matrix from Eqn. (76).

The principal subvectors $X_i^{\alpha\alpha}$ are the characteristic vectors of the system $M^{\alpha}\rightarrow$. Since such a scheme involves a zero equilibrium composition, there exists only one natural linear reaction pathway located in the positive octant of the vector space and coinciding with the directions of the vector $X_r^{\alpha\alpha}$. However, if the composition vector $a_x^{\alpha}(t)$ is located initially in the plane of the vectors $X_r^{\alpha\alpha}$ and $X_i^{\alpha\alpha}$, the movement of the system towards equilibrium is described by the equation

$$a_x^{\alpha}(t)=b_r^{\alpha}(t)X_r^{\alpha\alpha}+b_i^{\alpha}(t)X_i^{\alpha\alpha}. \tag{77}$$

When this curved pathway is projected onto the (1, 1, ..., 1) hyperplane, it is possible to obtain an artificial linear reaction pathway. Using a projection parallel to the vector $X_r^{\alpha\alpha}$, we obtain the equation for the artificial composition vector $\hat{a}(t)$:

$$\hat{a}^{\alpha}(t)=a^{\alpha}(t)+\delta(t)X_r^{\alpha\alpha}. \tag{78}$$

The scalar $\delta(t)$ is chosen so that

$$\delta(t)=1-\sum_{i=1}^{n^{\alpha}} a_i^{\alpha}(t). \tag{79}$$

The transformation of the subsystem A^{α} leads to a subsystem $\hat{M}^{\alpha}$ in which there are $n^{\alpha}-1$ artificial linear reaction pathways for each vector $X_i^{\alpha\alpha}$ with $i \neq r$. These artificial linear pathways can be found by the procedure used to find the natural linear pathways in a system of reversible reactions. Thus the following steps are necessary for the determination of the rate constants in the subsystem $M^{\alpha}\rightarrow$:

1. One must find the natural linear reaction pathway and the unique quasipositive characteristic vector $X_r^{\alpha\alpha}$. This can be done as described above when reversible reactions were considered.
2. The experimental reaction pathways are recalculated in terms of Eqns. (78) and (79), which gives rise to the artificial subsystems $\hat{M}^{\alpha}$.
3. The linear reaction pathways and the vectors $\alpha_{x_i}(0)$ must be found for the artificial subsystem $\hat{M}^{\alpha}$. This is again done by the procedure described above.
4. The vectors $X_i^{\alpha\alpha}$ with $i \neq r$ must be determined.

Since the vectors $\hat{a}_x^{\alpha}(0)$, $X_i^{\alpha\alpha}$, and $X_r^{\alpha\alpha}$ are coplanar, it is sufficient to determine the constant γ in the equation

$$X_i^{\alpha\alpha}=\hat{a}_x^{\alpha}(0)+\gamma X_r^{\alpha\alpha}. \tag{80}$$

Using the orthogonality relations, we obtain

$$\gamma=-\frac{[(X_r^{\alpha\alpha})^{T}(D^{\alpha})^{-1}a_x^{\alpha}(0)]}{[(X_r^{\alpha\alpha})^{T}(D^{\alpha})^{-1}(X_r^{\alpha\alpha})]}, \tag{81}$$

where the superscript T implies the transpose of a matrix; the matrix $(D^{\alpha})^{-1}$ is of the form

$$(D^{\alpha})^{-1}=\begin{pmatrix}1/a_1^{*} & & & & \\ & \cdot & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & 1/a_n^{*}\end{pmatrix}, \tag{82}$$

where a_i^{*} are the equilibrium concentrations in the absence of irreversible stages.

5. The eigenvalues must be determined.

For the subvector $X_r^{\alpha\alpha}$, located in positive octant of the space A^{α}, we can observe directly the rate of movement towards zero characteristic composition:

$$\hat{a}_x^{\alpha}(t)=b_r^{\alpha}(t)X_r^{\alpha\alpha}=b_r^{\alpha}(0)\cdot e^{\lambda_r^{\alpha}t}X_r^{\alpha\alpha}. \tag{83}$$

Consequently

$$\ln\frac{b_r^{\alpha}(t)}{b_r^{\alpha}(0)}=\lambda_r^{\alpha}t. \tag{84}$$

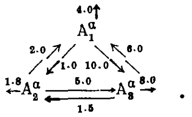
λ_r^{α} can therefore be found from the plot of $\ln[b_r^{\alpha}(t)/b_r^{\alpha}(0)]$ against t. However, this method cannot be applied to the subvectors $X_i^{\alpha\alpha}$ $(i \neq r)$, since they are not located in the positive octant of the vector space. On the other hand, we can determine the ratio $\lambda_i^{\alpha}/\lambda_r^{\alpha}$ from any curved pathway located in the plane of the vectors X_r and X_i.

The corresponding equation is

$$\frac{b_i^{\alpha}(t)}{b_r^{\alpha}(t)}=\left[\frac{b_r^{\alpha}(t)}{b_r^{\alpha}(0)}\right]^{\lambda_i^{\alpha}/\lambda_r^{\alpha}}. \tag{85}$$

Having plotted $\ln[b_i^{\alpha}(t)/b_i^{\alpha}(0)]$ against $\ln[b_r^{\alpha}(t)/b_r^{\alpha}(0)]$ we should obtain a straight line with a slope equal to $\lambda_i^{\alpha}/\lambda_r^{\alpha}$. Furthermore, Eqn. (85) provides a method for the determination of the relative rate constants from experimental composition data without the need to know λ_r^{α} and the contact time. However, if we determine only the relative characteristic numbers λ_i^{α} for each subsystem $M^{\alpha}\rightarrow$, then all the elements $K^{\alpha\alpha}$ will be referred to one of the constants within each subsystem of the reversible reactions. In order to obtain the final result, it is therefore necessary to reduce all the submatrices $K^{\alpha\alpha}$ to a single basis. The foregoing will be made clear by an example.

Example 3. Suppose that the following reaction scheme is specified:



(XX)

The rate constant matrix then assumes the following form:

$$K=\begin{pmatrix}-15.0 & 1.0 & 6.0\\ 1.0 & -8.8 & 1.5\\ 10.0 & 5.0 & -15.5\end{pmatrix}. \tag{86}$$

Table 3 presents several points along the reaction pathway, which corresponds to the initial composition

$$a^\alpha(0)=\begin{pmatrix}1\\0\\0\end{pmatrix}. \tag{87}$$

Table 3. Parallel projections for the system (XX).

t	$a^\alpha(t)$	$\sum_{i=1}^{n} a^\alpha(t)$	$\delta(t)$	$\delta(t)\,X_r^{\alpha\alpha}$	$\hat{a}^\alpha(t)$
0	$\begin{pmatrix}1\\0\\0\end{pmatrix}$	1.0	0	$\begin{pmatrix}0\\0\\0\end{pmatrix}$	$\begin{pmatrix}1\\0\\0\end{pmatrix}$
0.02	$\begin{pmatrix}0.7500\\0.0182\\0.1489\end{pmatrix}$	0.9171	0.0829	$\begin{pmatrix}0.0260\\0.0215\\0.0354\end{pmatrix}$	$\begin{pmatrix}0.7760\\0.0397\\0.1843\end{pmatrix}$
0.20	$\begin{pmatrix}0.1336\\0.0557\\0.1605\end{pmatrix}$	0.3498	0.6502	$\begin{pmatrix}0.2032\\0.1692\\0.2778\end{pmatrix}$	$\begin{pmatrix}0.3368\\0.2249\\0.4383\end{pmatrix}$

It also illustrates the course of the calculation for a parallel projection of the reaction pathway. The positively defined vector

$$X_r^{\alpha\alpha}=\begin{pmatrix}0.3126\\0.2602\\0.4272\end{pmatrix}, \tag{88}$$

to which corresponds a natural linear reaction pathway, is assumed to be known in these calculations. Fig. 12 illustrates artificial linear pathways for the system (XX). In our example, the matrix $(D^\alpha)^{-1}$ is

$$(D^\alpha)^{-1}=\begin{pmatrix}1/0.3158 & 0 & 0\\ 0 & 1/0.1579 & 0\\ 0 & 0 & 1/0.5263\end{pmatrix}. \tag{89}$$

We now determine the vector $X_2^{\alpha\alpha}$ from the initial composition for the linear section

$$\hat{a}_x^\alpha(0)=\begin{pmatrix}0.4510\\0\\0.549\end{pmatrix}. \tag{90}$$

We obtain from Eqn. (81)

$$\gamma=-\frac{0.8920}{1.0850}=-0.8221. \tag{91}$$

Eqn. (80) yields

$$X_2^{\alpha\alpha}=\begin{pmatrix}0.4510\\0\\0.5490\end{pmatrix}-0.8221\begin{pmatrix}0.3126\\0.2602\\0.4272\end{pmatrix}=\begin{pmatrix}0.1940\\-0.2139\\0.1978\end{pmatrix}. \tag{92}$$

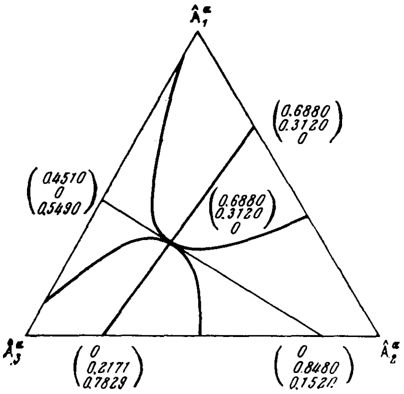


Figure 12. Artificial linear pathways for the system (XX).

The rate constant for irreversible reactions. In order to employ the above method for the determination of the individual constants for all irreversible reactions, it is necessary to determine the characteristic vectors for the systems containing both the main subvectors and the subvectors of the transitional systems. We shall consider initially two special cases: the system $M^\alpha \rightarrow M^\nu$ (where M^ν is a finite subsystem) and the open system

$$\begin{tikzcd} M^\alpha \arrow[r] \arrow[d] & M^\beta \arrow[d, "K^{\beta\alpha}\neq 0"'] \\ \text{when} & {} \end{tikzcd} \tag{XXI}$$

The system $M^\alpha \rightarrow M^\nu$ is closed and the equilibrium characteristic vector is

$$X_e^\nu=\begin{pmatrix}0\\X_e^{\nu\nu}\end{pmatrix}. \tag{93}$$

The system contains a unique natural linear reaction pathway corresponding to the vector X_r^α. We shall show below how to obtain artificial linear pathways corresponding to the vectors X_i^α $(i\neq r)$ by parallel projection. These linear pathways lie in a subspace of the composition space. We saw above that parallel projection gives rise to an artificial system $\hat{M}$ with the equilibrium vector $X_e^\alpha + CX_r^\alpha$.

The algorithm for the calculation of the rate constants for the system $M^\alpha \rightarrow M^\nu$ reduces to the following steps:

1. We find the natural linear reaction pathway and the positively defined vector X_r^α. The equilibrium vector X_e^ν is assumed to be known.

2. We consider the subsystem $M^{\alpha}\rightarrow$ and determine the subvectors $X_{i}^{\alpha\alpha}$ and the rate constants for the reversible reactions (see subsection D above).

3. We carry out a projection parallel to the vector X_{r}^{α} in accordance with the formula

$$\hat{a}(t)=a(t)+\delta(t)X_{r}^{\alpha},\tag{94}$$

where $\delta(t)$ is chosen so that the ith coordinate of the vector $\hat{a}(t)$ should be zero, i.e. $\hat{a}_{i}(t)=0$.

4. We find the equilibrium point in the artificial system $X_{e}^{\nu}+CX_{r}^{\alpha}$. The constant C is chosen on the basis of the condition that the ith coordinate of the equilibrium vector is equal to zero.

5. We find the artificial linear pathways and the vectors $\hat{a}_{i}(0)$.

6. We determine the vectors X_{i}^{α}, which requires the determination of the constants γ_1 and γ_2 in the equation

$$\begin{pmatrix}X_{i}^{\alpha\alpha}\\ X_{i}^{\nu\alpha}\end{pmatrix}=\gamma_1\begin{pmatrix}X_{r}^{\alpha\alpha}\\ X_{r}^{\nu\alpha}\end{pmatrix}+\gamma_2\left\{\begin{pmatrix}a_{x}^{\alpha}(0)\\ a_{x}^{\nu}(0)\end{pmatrix}-\begin{pmatrix}0\\ X_{e}^{\nu\nu}\end{pmatrix}-C\begin{pmatrix}X_{r}^{\alpha\alpha}\\ X_{r}^{\nu\alpha}\end{pmatrix}\right\}.\tag{95}$$

The constants γ_1 and γ_2 are determined from the vector equation

$$X_{i}^{\alpha\alpha}=\gamma_1X_{r}^{\alpha\alpha}+\gamma_2\{a_{x}^{\alpha}(0)-CX_{r}^{\alpha\alpha}\}\tag{96}$$

using the known subvectors $X_{r}^{\alpha\alpha}$ and $X_{i}^{\alpha\alpha}$.

7. The eigenvalues λ_{i}^{α} are determined in the study of the subsystem $M^{\alpha}\rightarrow$. The values of λ_{i}^{ν} are found when the subsystem M^{ν} is examined, as described in the discussion of reversible reactions.

Consider now the open system

$$\begin{tikzcd} M^{\alpha} \arrow[r] \arrow[d] & M^{\beta} \arrow[d] \\ {} & {} \end{tikzcd}\tag{XXII}$$

It was shown above that, when $|\lambda_{r}^{\alpha}|<|\lambda_{r}^{\beta}|$, the vector $X_{r}=\begin{matrix}0\\ X_{r}^{\beta\beta}\end{matrix}$ contains only positive elements. Depending on the relative eigenvalues, we should therefore project the reaction pathways parallel to X_{r}^{u} or X_{r}^{β}. Since natural linear pathways in the positive octant of the vector space correspond to positively defined vectors, the linear pathways should be found first and λ_{r}^{β} and λ_{r}^{α} should be determined. Assuming that this step has already been carried out, we shall consider two cases.

I. Let

$$|\lambda_{r}^{\alpha}|<|\lambda_{r}^{\beta}|.\tag{97}$$

(1) We set up an artificial subsystem by a projection parallel to X_{r}^{u} in accordance with the equation

$$\hat{a}^{u}(t)=a^{u}(t)+\delta(t)X_{r}^{u},\tag{98}$$

where the scalar $\delta(t)$ is chosen so that the sum of the elements $a(t)$ is unity.

(2) We determine the linear pathways in the artificial subsystems $a_{x_i}(0)$.

(3) We determine the vectors

$$X_{i}^{u}=\gamma_1\hat{a}_{x}(0)+\gamma_2X_{r}^{u}.\tag{99}$$

The constants γ_1 and γ_2 are determined from the known subvector $X_{i}^{\alpha\alpha}$, which is found beforehand by studying the subsystem $M^{\alpha}\rightarrow$.

II. Let

$$|\lambda_{r}^{\alpha}|>|\lambda_{r}^{\beta}|.$$

(1) Projection parallel to the vector X_{r}^{β} leads to the equation

$$\hat{a}^{u}(t)=a^{u}(t)+\delta_1(t)X_{r}^{\beta},\tag{100}$$

where $\delta_1(t)$ is chosen in such a way that the sum of the coordinates $\hat{a}_{i}^{u}(t)$ is unity. Such projection leads to an artificial closed system of the type $\hat{M}^{\alpha}\rightarrow\hat{M}^{\beta}$, in which there is a unique linear reaction pathway in the positive octant of the vector space and a unique characteristic vector X_{r}^{u} without negative elements.

(2) We find the linear reaction pathway and the vector $\hat{a}_{x}^{u}(0)$.

(3) We determine the vector X_2 from the equation

$$X_{2}^{u}=\begin{pmatrix}\hat{a}_{x}^{\alpha}(0)\\ \hat{a}_{x}^{\beta}(0)\end{pmatrix}+\gamma\begin{pmatrix}0\\ X_{r}^{\beta\beta}\end{pmatrix}.\tag{101}$$

The coefficient γ is determined by studying the curved pathway in the hyperplane of the vectors X_{r}^{u} and X_{r}^{β}. The reaction pathway in this hyperplane is given by the equation

$$a(t)=b_{r}^{\alpha}(t)X_{r}^{u}+b_{r}^{\beta}(t)X_{r}^{\beta}.\tag{102}$$

Using Eqn. (101), it can be shown that

$$b_{r}^{\alpha}(t)=e^{\lambda_{r}^{\alpha}t};\ b_{r}^{\beta}(t)=-\gamma e^{\lambda_{r}^{\beta}t}.\tag{103}$$

It follows from Eqns. (102) and (103) that

$$F_1=\left(\sum a_{l}^{\beta}(t)-e^{\lambda_{r}^{\alpha}t}\sum a_{x_l}^{\beta}(0)\right)=\gamma F_2=\gamma\left(e^{\lambda_{r}^{\alpha}t}-e^{\lambda_{2}^{\beta}t}\right).\tag{104}$$

Since λ_{r}^{α} and λ_{r}^{β} may be assumed to have been determined from the study of the subsystems $M^{\alpha}\rightarrow$, the constant γ a can be found from the slope of the linear plot of F_1 against F_2.

(4) In order to determine the characteristic vectors X_{i}^{u}, where $i\neq r$, it is necessary to carry out a second projection using the vector $X_{r}^{u}-X_{r}^{\beta}$ in accordance with the formula

$$\hat{\hat{a}}^{u}(t)=\hat{a}^{u}(t)+\delta_2(t)(X_{r}^{u}-X_{r}^{\beta}),\tag{105}$$

where $\delta_2(t)$ is chosen so that one of the coordinates of the vector $\hat{\hat{a}}^{u}(t)$ is zero and the others are positive.

(5) We find the characteristic vectors X_{i}^{u}. For this purpose, it is necessary to determine the three constants in the equation

$$X_{2}^{u}=\gamma_1\begin{pmatrix}\hat{\hat{a}}_{x}^{\alpha}(0)\\ \hat{\hat{a}}_{x}^{\beta}(0)\end{pmatrix}+\gamma_2\begin{pmatrix}X_{r}^{\alpha\alpha}\\ X_{r}^{\beta\alpha}\end{pmatrix}+\gamma_3\begin{pmatrix}0\\ X_{r}^{\beta\beta}\end{pmatrix}.\tag{106}$$

Since the subvector $X_{2}^{\alpha\alpha}$ may be regarded as known, a system of equations for the determination of γ_1 and γ_2 follows from the first row of Eqn. (106):

$$X_{2}^{\alpha\alpha}=\gamma_1\hat{\hat{a}}^{\alpha}(0)+\gamma_2X_{r}^{\alpha\alpha}.\tag{107}$$

The curved pathway in the subspace stretched over the three vectors X_{i}^{u}, X_{r}^{u}, and X_{r}^{β} may be used to determine γ_3:

$$a(t)=b_{i}^{\alpha}(t)X_{i}^{u}+b_{r}^{\alpha}(t)X_{r}^{u}+b_{r}^{\beta}(t)X_{r}^{\beta};\tag{108}$$

and it can be shown that in our case

$$b_{i}^{\alpha}(t)=\frac{1}{\gamma_1}e^{-\lambda_{1}^{\alpha}t},$$

$$b_{r}^{\alpha}(t)=-\frac{\gamma_2}{\gamma_1}e^{-\lambda_{r}^{\alpha}t},$$

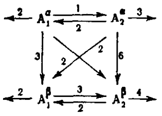
$$b_{r}^{\beta}(t)=-\frac{\gamma_3}{\gamma_1}e^{\lambda_{r}^{\beta}t}.$$

The constant γ_3 can be found from the slope of the linear plot of F_3 against F_4, where

$$F_3=\gamma_1\Big[\sum_i a_i^{\beta}(t)-e^{\lambda_i^{\alpha}t}\sum_i \hat{\hat{a}}_x^{\beta}(0)\Big]-\gamma_2[e^{\lambda_i^{\alpha}t}-e^{\lambda_r^{\alpha}t}]X_r^{\beta\alpha};$$
$$F_4=[e^{\lambda_i^{\alpha}t}-e^{\lambda_r^{\beta}t}]\cdot\sum X_{ri}^{\beta\beta}. \qquad (109)$$

The procedure for the calculation of the constants can be made clear by the following artificial example[29].

Example 4. Consider the scheme



(XXIII)

The rate constant matrix is

$$K=\begin{pmatrix}-8 & 2 & 0 & 0\\ 1 & -13 & 0 & 0\\ 3 & 2 & -5 & 2\\ 2 & 6 & 3 & -6\end{pmatrix}, \qquad (110)$$

$$\lambda_r^{\alpha}=-7.6277 \text{ and } \lambda_r^{\beta}=-3.0.$$

and the characteristic vector matrix assumes the following form:

$$X=\begin{pmatrix}-2.7446 & 8.7445 & 0 & 0\\ -0.5109 & -3.4891 & 0 & 0\\ 1.1861 & -1.6861 & 0.5 & -2\\ 3.0694 & 17.4307 & 0.5 & 3\end{pmatrix}. \qquad (111)$$

Fig. 13 illustrates the reaction pathways for the initial composition

$$\begin{pmatrix}0.5341\\0.0994\\0.3665\\0\end{pmatrix}.$$

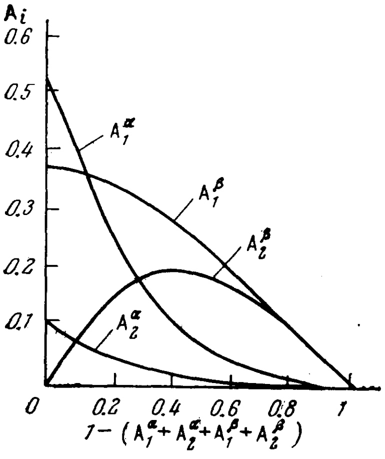


Figure 13. Reaction pathway for the system (XXIII).

Table 4 presents the calculations for a projection parallel to the vector

$$X_r^{\beta}=\begin{pmatrix}0\\X_r^{\beta\beta}\end{pmatrix}=\begin{pmatrix}0\\0\\0.5\\0.5\end{pmatrix}. \qquad (112)$$

The artificial linear reaction pathway for the initial composition

$$\begin{pmatrix}0.5341\\0.0994\\0.3665\\0\end{pmatrix}$$

is illustrated in Fig. 14.

Table 4.

t	$a^u(t)$	$\sum_i a_i^u(t)$	$\delta_1(t)$	$\delta_1(t)X_r^{\beta}$	$\hat{a}^u(t)$
0	$\begin{pmatrix}0.5341\\0.0944\\0.3665\\0\end{pmatrix}$	1.0	0	$\begin{pmatrix}0\\0\\0\\0\end{pmatrix}$	$\begin{pmatrix}0.5341\\0.0944\\0.3665\\0\end{pmatrix}$
0,05	$\begin{pmatrix}0.3644\\0.0653\\0.3561\\0.3552\end{pmatrix}$	0.8910	0.1090	$\begin{pmatrix}0\\0\\0.0545\\0.0545\end{pmatrix}$	$\begin{pmatrix}0.3644\\0.0553\\0.4106\\0.1597\end{pmatrix}$
0.10	$\begin{pmatrix}0.2488\\0.0450\\0.3342\\0.1626\end{pmatrix}$	0.7906	0.2094	$\begin{pmatrix}0\\0\\0.1047\\0.1047\end{pmatrix}$	$\begin{pmatrix}0.2488\\0.0450\\0.4389\\0.2673\end{pmatrix}$
0.15	$\begin{pmatrix}0.1698\\0.0309\\0.3066\\0.1893\end{pmatrix}$	0.6966	0 0.3034	$\begin{pmatrix}0\\0\\0.1517\\0.1517\end{pmatrix}$	$\begin{pmatrix}0.1698\\0.0309\\0.4583\\0.3410\end{pmatrix}$
0.35	$\begin{pmatrix}0.0369\\0.0068\\0.1923\\0.1668\end{pmatrix}$	0.4028	0.5972	$\begin{pmatrix}0\\0\\0.2986\\0.2986\end{pmatrix}$	$\begin{pmatrix}0.0369\\0.0068\\0.4909\\0.4654\end{pmatrix}$

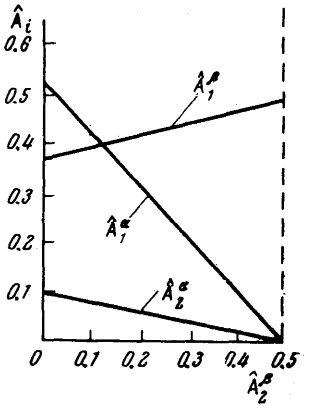


Figure 14. Artificial linear reaction pathway for the system (XXIII).

The functions F_1 and F_2 are calculated from Eqn. (104). A linear plot of F_1 against F_2 is obtained, whose slope yields $\gamma=-1.189$. We now calculate X_r^u from Eqn. (99):

$$X_r^u=\begin{pmatrix}0.5341\\0.0994\\0.3665\\0\end{pmatrix}-1.189\begin{pmatrix}0\\0\\0.5\\0.5\end{pmatrix}=\begin{pmatrix}0.5341\\0.0994\\-0.2280\\-0.5945\end{pmatrix}. \qquad (113$$

The vector X^{u}_{r} differs only by its length and sign from the first column of the matrix X [Eqn. (111)].

In order to determine X_2, we make use of a further projection, but this time the projection is parallel to the vector $X^{u}_{r} - X^{\beta}_{r}$. The course of the calculations is illustrated in Table 5.

Table 5.

t	$a^{u}(t)$	$\delta_1(t)$	$\hat{a}^{u}(t)$	$\delta_2(t)$	$\hat{\hat{a}}^{u}(t)$
0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$	0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$	0	$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$
0.06	$\begin{pmatrix}0.0321\\0.2301\\0.4199\\0.1737\end{pmatrix}$	0.1442	$\begin{pmatrix}0.0321\\0.2301\\0.4920\\0.2458\end{pmatrix}$	—0.0957	$\begin{pmatrix}0.2947\\0.2790\\0.4263\\0\end{pmatrix}$
0.20	$\begin{pmatrix}0.0259\\0.0393\\0.2832\\0.2310\end{pmatrix}$	0.4206	$\begin{pmatrix}0.0259\\0.0393\\0.4935\\0.4413\end{pmatrix}$	—0.1718	$\begin{pmatrix}0.4973\\0.1270\\0.3757\\0\end{pmatrix}$

The reaction pathway for the initial composition

$$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$$

is illustrated in Fig. 15. Fig. 16 presents an artificial linear pathway. We shall now determine the constant of the equation

$$X^{u}_{i} = \begin{pmatrix}X^{\alpha\alpha}_{i}\\X^{\beta\alpha}_{i}\end{pmatrix} = \gamma_1\begin{pmatrix}\hat{\hat{a}}^{\alpha}_{x}(0)\\\hat{\hat{a}}^{\beta}_{x}(0)\end{pmatrix} + \gamma_2\begin{pmatrix}X^{\alpha\alpha}_{r}\\X^{\beta\alpha}_{r}\end{pmatrix} + \gamma_3\begin{pmatrix}0\\X^{\beta\beta}_{r}\end{pmatrix}. \qquad (114)$$

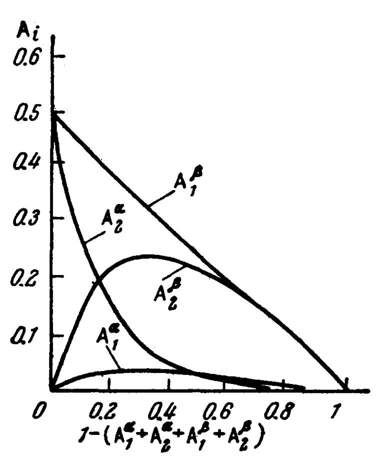


Figure 15. Reaction pathway for the system (XXIII).

Using the known subvectors $X^{\alpha\alpha}_{r}$ and $X^{\alpha\alpha}_{2}$, we obtain the following system of equations:

$$X^{\alpha\alpha}_{2} = \gamma_1\hat{\hat{a}}^{\alpha}_{x}(0) + \gamma_2 X^{\alpha\alpha}_{r} = \begin{pmatrix}-0.5931\\1.5931\end{pmatrix} + \gamma_1\begin{pmatrix}0\\0.5\end{pmatrix} + \gamma_2\begin{pmatrix}-2.7446\\-0.5109\end{pmatrix}. \qquad (115)$$

It follows from Eqn. (115) that $\gamma_1 = 3.4069$ and $\gamma_2 = 0.2161$. γ_3 is determined from the plot of F_3 against F_4. F_3 and F_4 are calculated from Eqns. (109) and $\gamma_3 = -3.691$ is found. We now determine

$$X^{u}_{2} = 3.4069\begin{pmatrix}0\\0.5000\\-0.5000\\0\end{pmatrix} + 0.21\begin{pmatrix}-2.7446\\0.5109\\1.1861\\3.0694\end{pmatrix} - 3.691\begin{pmatrix}0\\0\\0.5\\0.5\end{pmatrix} = \begin{pmatrix}-0.5931\\1.5931\\0.1142\\-1.1824\end{pmatrix}.$$

It is readily seen that X^{u}_{2} is identical with the second column of the matrix X apart from the length and sign.

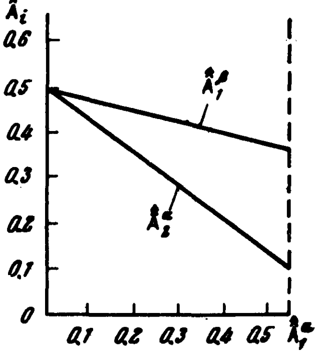


Figure 16. Artificial linear reaction pathway for the system (XXIII); initial composition.

$$\begin{pmatrix}0\\0.5\\0.5\\0\end{pmatrix}$$

4. THE GENERAL CHARACTERISTICS OF FIRST-ORDER REACTIONS

We examined above systems of reversible first-order reactions and systems involving certain irreversible stages. In both cases we employed the principle of detailed balance or its corollaries, which can be found by considering irreversible stages as the limiting cases of reversible reactions obtained on decreasing the rates of the corresponding transitions. However, there exist systems of pseudofirst order, to which the principle of detailed balance is in general inapplicable. We shall consider initially certain examples of such systems[30].

Example 5.

$$\begin{aligned}&A_1 + B_1 \rightleftarrows A_2 + B_2\ ;\\&A_2 + B_3 \rightleftarrows A_3 + B_4\ ;\\&A_3 + B_5 \rightleftarrows A_1 + B_6\ .\end{aligned} \qquad (XXIV)$$

If the reactions are carried out in a closed system, the usual thermodynamic conditions are valid. On the other hand, when the system contains an excess of substances

B, the reactions can be described by the equivalent pseudofirst order scheme:

$$A_1 \rightleftarrows A_2;\ A_2 \rightleftarrows A_3;\ A_3 \rightleftarrows A_4 \qquad \text{(XXV)}$$

One can then speak only of steady-state conditions. The Wegsheider conditions[18] may therefore not in fact hold for the matrix.

Example 6. Consider copolymerisation reactions, which can be described sometimes by first-order systems. We denote by $P_i(\nu)$ a polymer of type i with a chain length ν and by M_j a monomer of type j. The reaction mechanism can be formulated thus:

$$P_i(\nu) + M_j \to P_j(\nu + 1). \qquad (116)$$

The second-order reaction constant will be designated by k_{ij}. If the monomer concentration does not change, the process can be described by a system of unimolecular reactions with constants which depend on the monomer concentration. The diagonal elements of the kinetic matrix K then possess physical significance. The principle of detailed balance does not hold in such a system. Polymerisation kinetics have been examined in a number of studies[31-33].

Example 7. Suppose that the process takes place on a discretely inhomogeneous catalyst surface with two types of centres. A system of reactions with the kinetic matrices K_1 and K_2 takes place at each type of centres. Then the overall transformation can also be described by a first-order equation with the matrix $\lambda K_1 + (1 - \lambda)K_2$, where λ is the fraction of centres of the first type on the catalyst surface. It can be easily shown that, even if the principle of detailed balance holds for each set of centres, it may not hold for the system as a whole. In the specific instance where the matrices K_1 and K_2 have identical equilibrium vectors, the principle of detailed balance holds for the entire system. This can be readily understood, since in the latter case a thermodynamic equilibrium is established in the steady-state and the thermodynamic conditions are the same for both types of centres. On the other hand, when one is dealing with a system of pseudofirst order, there is no thermodynamic equilibrium and the steady-state conditions may be different for each type of centre. This factor is extremely important for the kinetics of complex reactions on polyfunctional catalysts[34-37].

Example 8. Consider the class of first-order reactions which have been called[30] "bound". This class includes systems containing cycles of irreversible reactions which we previously excluded from consideration. We introduce the following definitions. We call a substance A_i the descendant of A_j if a sequence of reactions $A_j \to A_k \to \ldots A_i$ with strictly positive constants exists. The system of unimolecular reactions is called bound if each substance is the descendant of another. For example, the system $A_1 \rightleftharpoons A_2 \to A_3$ is a bound system of an L-system. The system $A_1 \rightleftharpoons A_2$, $A_3 \rightleftharpoons A_4$ is not bound. A system of reversible reactions is an L-system if it cannot be subdivided into subsystems between which there is no interaction. The following two schemes do not belong to the L-class:

$$A_1 \rightleftarrows A_2 \to A_3 \rightleftarrows A_4\,; \qquad \text{(XXVI)}$$

$$\begin{tikzcd} A_1 \arrow[r] \arrow[rr, bend right] & A_2 \arrow[r] & A_3; & A_4 \arrow[r, shift left] & A_5 . \arrow[l, shift left] \end{tikzcd} \qquad \text{(XXVII)}$$

If the system can be subdivided into ν subsystems, each of which is an L-system, it belongs to the class L_ν. The following results have been obtained for L-systems.

1. All L-systems have a unique positively defined equilibrium vector.
2. A positively defined equilibrium vector exists when and only when the system of unimolecular reactions belong to the class L_ν. The multiplicity of the zeroth eigenvalue of the kinetic matrix is ν.
3. All the eigenvalues of the kinetic matrix (other than the zeroth eigenvalue) have negative real components and are located on a complex plane in a circle $|z + r| \leqslant r$, where r is the maximum modulus of the diagonal elements of the matrix K.[30] This assertion can be proved by the Perron theorem familiar in matrix theory[38].

Thus, in contrast to the systems of reversible reactions discussed above, decaying oscillations are possible in L-systems containing cycles. The introduction of non-linear stages into these systems leads to non-decaying auto-oscillations[39-41].

5. Group Kinetics

An enormous number of substances are sometimes involved simultaneously in complex systems, which precludes not only kinetic calculations on individual reactions but also even a simple chemical analysis of such mixtures. It is therefore necessary to subdivide substances into definite classes and to investigate the interactions between individual classes. For example, in the cracking of petroleum, hydrocarbons are subdivided into olefins, paraffins, naphthenes, and aromatic compounds. However, it is by no means always clear to what extent this distorts the kinetic relations and in what cases the subdivision of the reactants into groups is legitimate. An attempt has been made[42,43] to answer these questions in relation to systems of unimolecular reactions. We shall assume that conditions (14), formulated in the definition of a system of reversible reactions, have been fulfilled. We introduce a linear transformation of an n-dimensional vector composition space into an $\hat{n}$-dimensional space where $\hat{n} < n$. Such a transformation is achieved with the aid of a rectangular $\hat{n} \times n$ matrix M with the rank $\hat{n}$:

$$\hat{a} = Ma. \qquad (117)$$

In the simplest case this transformation can be represented as projection. Three substances can be divided into two classes (Fig. 17):

$$\hat{a}_1 = a_1 + a_2,$$
$$\hat{a}_2 = a_3. \qquad (118)$$

In this case, the transformation matrix M is

$$M = \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (119)$$

In this transformation the same vector $\hat{a}$ corresponds to vectors a' and a'' (see Fig. 17). We now introduce certain definitions.

Definition 5. Vectors a and a' will be called equivalent if the equality

$$Ma = Ma' \qquad (120)$$

holds. In an abbreviated form, Eqn. (120) can be written in the form

$$a \simeq a'.$$

Definition 6. The system of unimolecular reactions $da/dt = Ka$ is called exactly divisible into classes if, after transforming the composition space with the matrix $M : \hat{a} = Ma$, the kinetics can be described by the equation

$$\frac{d\hat{a}}{dt} = \hat{K}\hat{a}\,, \tag{121}$$

where $\hat{K}$ is a matrix.

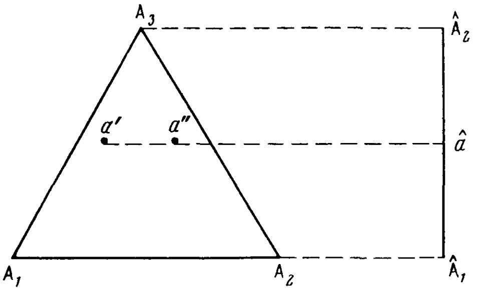


Figure 17. Transformation of the three-dimensional space specified by the matrix

$$\begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

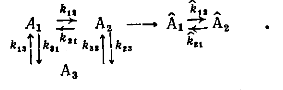
If the initial kinetic matrix has the dimensions $n \times n$, then the matrix $\hat{K}$ has the dimensions $m \times n$, where $m < n$. We shall now formulate the necessary and sufficient conditions under which the system is exactly divisible into classes.

Theorem 9. For the system to be exactly divisible into classes, the following conditions is necessary and sufficient:

$$MK = \hat{K}M, \tag{122}$$

where M is an $n \times m$ matrix. We shall make clear the significance of this condition in terms of examples. Consider a three-component system of reversible reciprocal reactions A_1, A_2, and A_3. We shall combine A_1 and A_2 in one class, while the second class will consist of A_3. This yields a two-component system:

Example 9.



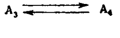
(XXVIII)

The matrix M for such a subdivision into classes was quoted above [matrix (119)]. The conditions (120) are

$$k_{31} = k_{32} = k_{13} + k_{23} = \hat{k}_{21} = \hat{k}_{12}. \tag{123}$$

We shall consider yet another example.

Example 10.



(XXIX)

We combine A_1 and A_2 in the first class and A_3 and A_4 in the second class. The equivalent scheme is the same as in the previous case:

$$\hat{A}_1 \underset{\hat{k}_{21}}{\overset{\hat{k}_{12}}{\rightleftarrows}} \hat{A}_2\,.$$

The conditions (120) then become

$$\begin{gathered} k_{31} + k_{41} = k_{32} + k_{42} = \hat{k}_{21}\,; \\ k_{13} + k_{23} = k_{14} + k_{24} = \hat{k}_{12}. \end{gathered} \tag{124}$$

Thus the conditions (120) impose sufficiently rigid limitations on the rate constants.

It has been shown[37] that the composition $\hat{a}(t)$ for systems divisible into classes can be calculated both from kinetic $a(t)$ curves and from the matrix K, i.e.

$$\hat{a}(t) = Me^{-Kt}a(0) = e^{-\hat{K}t}Ma(0). \tag{125}$$

This relation yields yet another definition of systems exactly divisible into classes.

Definition 7. A system of unimolecular reactions is called exactly divisible into classes if equivalence is maintained for the reaction pathways for each pair of M-equivalent vectors $a(0)$ and $a'(0)$. In other words, it follows from $a(0) \sim a'(0)$ that $a(t) \sim a'(t)$.

A consequence of this definition is that we should obtain a single reaction pathway $\hat{a}(t)$ in the transformed three-component system in experiments with the initial compositions (1, 0, 0) and (0, 1, 0) when the substances A_1 and A_2 are combined in one class. Different reaction pathways are of course obtained in the initial composition space. This can be used for experimental tests of the possibility of the subdivision of the system into classes. Suppose that the first three components in a system of five components are combined in one class and the fourth and fifth components are combined in the second class. The experiment is carried out for the initial composition (1, 0, 0, 0, 0). We determine the kinetic relations

$$\begin{gathered} \hat{a}_1(t) = a_1(t) + a_2(t) + a_3(t), \\ \hat{a}_2(t) = a_4(t) + a_5(t). \end{gathered} \tag{126}$$

We then repeat the experiment with the initial compositions (0, 1, 0, 0, 0) and (0, 0, 1, 0, 0). If we obtain similar relations $a_1(t)$ in all three experiments, the combination of substances A_1, A_2, and A_3 in a single class is legitimate. After this, it is possible to carry out experiments with the compositions (0, 0, 0, 1, 0) and (0, 0, 0, 0, 1). If the relations $\hat{a}_2(t)$ are the same in these experiments, the substances A_4 and A_5 can be combined in a single class.

We shall now consider how the characteristic vectors vary when the dimensions of the vector space are diminished on subdivision into classes.

Theorem 10. If X_i is the eigenvector of the rate constant matrix for a system which is exactly divisible into classes, corresponding to the eigenvalue λ_i, then the vector MX_i is zero or is the eigenvector of the matrix $\hat{K}$ with the same eigenvalue λ_i.

Thus, when the matrix K has n eigenvectors, the matrix $\hat{K}$ has $\hat{n}$ eigenvectors for the same values of λ_i and the equality $MX_i = 0$ hold for $n - \hat{n}$ vectors. Thus, by studying the reaction pathways in the space A_n, it is possible to determine $\hat{n}$ eigenvectors $X_i = MX_i$ for the exact values of λ_i. The remaining eigenvectors of the initial system cannot be determined.

The subdivision of complex systems into classes taking into account diffusion has also been examined[42]. An approach has been described[43], in terms of the above definitions, to the study of unimolecular systems which cannot be exactly subdivided into classes. However, this can be done only approximately. Expressions are given whereby it is possible to estimate the errors arising in the approximate subdivision of complex systems into classes containing several substances.

In the present section, we have considered only those investigations in which an attempt has been made to approach group kinetics from the standpoint of the general theory of unimolecular reactions. Naturally, other approaches to the problem are also possible. For example, reactants can be represented by mixtures with continuous compositions[44-46]. The extensive literature on this problem cannot be discussed here.

III. AN OUTLINE OF THE STRUCTURE OF NON-LINEAR SYSTEMS

1. Canonical Forms

It is possible to find simple canonical forms for linear systems which are convenient for the solution of equations and the analysis of the structure. For non-linear systems of complex reaction, the situation is much more involved. Consider a non-linear system of complex reactions[27]:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = \mathrm{f}^i(x^1, \ldots x^n);\ i = 1, \ldots n. \tag{127}$$

In the general case, there exists a non-linear transformation leading to the system (127) in the canonical form:

$$\begin{aligned} &\frac{\mathrm{d}y^1}{\mathrm{d}t} = g(y^1, \ldots y^n), \\ &\frac{\mathrm{d}y^i}{\mathrm{d}t} = 0;\ i = 2, \ldots n. \end{aligned} \tag{128}$$

However, there is no general method for deducing these transformations. We shall consider a system of chemical kinetic equations obtained in accordance with the Law of Mass Action. For reactions whose order is not greater than the third, one can write

$$\frac{\mathrm{d}x^i}{\mathrm{d}t} = \sum_j a^i_j x^j + \sum_{k,j} b_{jk} x^j x^k + \sum_{j,k,p} c_{jkp} x^j x^k x^p. \tag{129}$$

The first term of Eqn. (129) corresponds to first-order reactions and the second term describes second-order reactions. It can be shown[47,48] that equations of type (129) with up to sth order terms can be reduced to homogeneous sth order equations. Henceforth we shall consider only homogeneous systems having specified

$$\frac{\mathrm{d}X}{\mathrm{d}t} = P_n(X), \tag{130}$$

where $P_n(X)$ is the polynomial form of the vector X.[49] For a polylinear operator, there exist canonical forms which can be solved.

1. $P_n(X)$ is a semilinear operator:

$$\begin{gathered} P_n(X + Y) = P_n(X) + P_n(Y), \\ P_n(\alpha X) = \mathrm{f}(\alpha) P_n(X). \end{gathered} \tag{131}$$

This form arises, for example, for the scheme

$$\begin{gathered} 2\,\mathrm{A} \rightarrow \mathrm{B} \quad , \\ 3\,\mathrm{C} \rightarrow \mathrm{D} \quad . \end{gathered}$$

2. The triangular scheme:

$$2\,\mathrm{A} \rightarrow 2\,\mathrm{B} \rightarrow 2\,\mathrm{C} \quad .$$

3. The scheme

$$\begin{gathered} \mathrm{A}_1 + \mathrm{A}_2 \xrightarrow{k_1} \mathrm{A}_3 \ , \\ \mathrm{A}_1 + \mathrm{A}_3 \xrightarrow{k_2} \mathrm{A}_4 \end{gathered} \tag{XXX}$$

and the more complex scheme

$$\begin{gathered} \mathrm{A}_1 + \mathrm{A}_2 \rightarrow \mathrm{A}_3 \quad , \\ \mathrm{A}_3 + \mathrm{A}_2 \rightarrow \mathrm{A}_4 \quad , \\ \mathrm{A}_5 + \mathrm{A}_2 \rightarrow \mathrm{A}_6 \quad , \\ \mathrm{A}_6 + \mathrm{A}_2 \rightarrow \mathrm{A}_7 \end{gathered} \tag{XXXI}$$

have also been considered[50,51]. Unfortunately other canonical forms do not permit a solution of the initial system. The problem of the canonical forms of second-order equations has still been little studied.

2. Linear Reaction Pathways

For a linear system, a linear reaction pathway is specified by the formula

$$X(t) = X_e + \alpha(t) Y, \tag{132}$$

where X_e is the equilibrium vector. We shall consider a second-order homogeneous system:

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = B(X, X). \tag{133}$$

The possibility of the existence of linear reaction pathways will now be elucidated. Having substituted Eqn. (132) in Eqn. (133), we obtain

$$Y \frac{\mathrm{d}\alpha}{\mathrm{d}t} = B(X_e, X_e) + 2\alpha B(X_e, Y) + \alpha^2 B(Y, Y). \tag{134}$$

The first term is zero, since at equilibrium $\mathrm{d}\boldsymbol{X}_e/\mathrm{d}t = 0$. For Eqn. (134) to hold, it is necessary and sufficient that the following conditions should be fulfilled:

$$B(X_e, Y) = \beta Y, \tag{135}$$

$$B(Y, Y) = \lambda Y. \tag{136}$$

These conditions are rarely fulfilled, but they are valid in some cases, for example for the scheme $2\mathrm{A} \rightleftharpoons 2\mathrm{B} \rightleftharpoons 2\mathrm{C}$. For closed systems, linear pathways are rare. However, for systems with irreversible stages involving open subsystems, this is not the case.

Consider the system

$$2\,\mathrm{A} \rightarrow \mathrm{C};\ 2\mathrm{B} \rightarrow \mathrm{E};\ \mathrm{A} + \mathrm{B} \rightarrow \mathrm{D}.$$

It contains the open subsystem (A, B). When $t \rightarrow \infty$, we have $c_A \rightarrow 0$ and $c_B \rightarrow 0$. In the general case of a system with irreversible stages, the equilibrium vector is $X_e(0, 0, 0, \ldots, x_e^{n+1}, x_e^n)$. When an m-dimensional space is considered, the equilibrium point coincides with the origin of coordinates. For such subsystems, linear pathways are possible, since $B(X_e, Y) = 0$ and it is only necessary that $B(Y, Y) = \lambda Y$; for a homogeneous sth order system, condition (136) assumes the following form:

$$P_s(\alpha X) = \alpha^s P_s(X). \tag{137}$$

The following Wei theorem is valid:

Theorem 11. For chemical reactions involving any number of components, and of any homogeneous order, the equilibrium point either does not coincide with the origin of coordinates or there is at least one pathway in the positive octant of the vector space.

We shall now discuss the problem of the number of possible linear pathways. The number of such pathways is equal to the number of the roots of the equation

$$P_s(aX)=a^s\lambda X. \tag{138}$$

We found above that for linear systems there can be not more than n independent eigenvectors or that an infinite number of eigenvectors corresponds to a single eigenvalue. In the non-linear case, reliable results have been obtained mainly for a two-component system. Table 6 presents the maximum number of linear pathways as a function of the number of components and the order of the reaction.

Table 6. Number of possible linear reaction pathways.

No. of components	Reaction order				
	1	2	3	4	5
2	2	3	4	5	6
3	3	(8)	—	—	—

It is seen from these results that analysis of linear reaction pathways in non-linear systems cannot yield far-reaching results similar to those obtained for unimolecular reactions. At the same time, some of the theorems quoted above are useful also in the consideration of non-linear systems. In particular, they are useful in the analysis of stability, since Lyapunov theorems reduce the problem to the analysis of the stability of the linearised system. Thus the impossibility of non-decaying oscillations in the vicinity of thermodynamic equilibrium follows from theorem 2. A detailed proof of this assertion can be found in Zhabotinskii's book[39]. Interesting communications on the qualitative theory of chemical kinetic equations have been published very recently[52-56]. However, their discussion is outside the scope of the present review.

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Ion-Molecule Reactions Initiated by the β-Decomposition of Tritium in Tritiated Compounds

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Ion-molecule reactions initiated by the β-decomposition of tritium in various compounds are examined and a systematic account is given. The theoretical and experimental foundations of the radiochemical method for the investigation of this important type of chemical interactions are described. The ion-molecule reactions investigated are combined in two groups: the reactions of the ions HeT^+ and the reactions of carbonium ions. Conclusions concerning the reactivity of the intermediate species, the mechanisms of their interaction with various substances, and the prospects for the utilisation of the radiochemical method of investigating ion-molecule reactions are reached on the basis of the experimental results presented.
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I. INTRODUCTION

As early as the end of the last century, the existence of molecular ions was discovered from the study of the electrical conductivities of flames and gases subjected to an electrical discharge. In 1905, Langevin[1] and subsequently also other investigators[2] attempted a theoretical development of models of the gas-phase interaction of charged species with neutral molecules. However, the first experimental study[3] specially devoted to ion-molecule reactions was not published until 1952. During the two decades elapsed since its publication, there has been a sharp growth of intensity of research in this field. In the USA alone, more than one hundred papers have been published annually during the last few years on ion-molecule reactions and the expenditure by the state on this research exceeds at the present time 2 500 000 dollars annually[4].

The interest in ion-molecule reactions is due to the fact that the knowledge of the mechanism, thermochemistry, and kinetics of these interactions is extremely important for the understanding of the processes developing under the influence of radiation and light, in the flame, in electrical discharges, in mass spectrometers, in the upper layers of Earth's atmosphere, in the atmospheres of other planets, and in heterolytic organic reactions. Thus, for example, as early as the beginning of this century, it was established that certain organic substances are capable of dissociating into molecular ions[5]. Numerous subsequent investigations by organic chemists showed that the majority (approximately 60%) of organic reactions proceed via a stage involving the formation of charged molecular species—carbonium ions. The processes accompanying the interaction of radiation or light with matter also take place with participation of ionised species. The hypothesis of the occurrence of ion-molecule reactions in radiation processes, put forward by Lind[6] as early as 1912, has now been widely adopted in radiation chemistry[7-11]. Bimolecular reactions between ions and molecules have been observed in mass spectrometry as secondary processes already in the first instruments. However, these reactions were regarded for a long time as fundamental obstacles to the development of analytical mass spectrometry[12-14]. For this reason, despite their early observation, the systematic study of these reactions did not begin until the 1960s.[3,15-17] Ion-molecule reactions also play an important role in astrochemistry. For example, Libby[18] suggested that the ion-molecule reactions developing in Jupiter's atmosphere may give rise to "petroleum rain"†.

Ion-molecule reactions are studied at present mainly by the following methods: (1) mass spectrometry; (2) ion-cyclotron resonance; (3) the method of the total elimination of charge; (4) the discharge technique; (5) the radiochemical method. With the exception of the last procedure, all these methods have been discussed in detail in numerous reviews of ion-molecule reactions[20-40] and also in a review[41] specially devoted to the experimental techniques for the investigation of these processes. The lack in the above publications of information about the radiochemical method for the investigation of ion-molecule reactions can apparently be accounted for by the fact that the first studies in this field were begun less than ten years ago[42-45]. Despite the comparatively recent introduction of the method, it has now been used successfully in more than 30 investigations.

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† This striking picture of the atmospheric phenomena on Jupiter was described by Libby at a lecture devoted to the 50th anniversary of the National Scientific Council of Canada in 1966. The arguments presented reduced to the following. The components of Jupiter's atmosphere are known to be hydrogen and methane, which ionise under the influence of intense cosmic radiation. The H_2^+ and CH_4^+ ions generated thereby react with methane, forming the highly reactive species CH_5^+, which is capable of giving rise to the synthesis of heavy hydrocarbons[19].

The method is based on a fundamentally new procedure for the initiation of ion–molecule reactions, consisting in the generation of molecular ions by the spontaneous nuclear-chemical transformation of tritiated compounds:

$$\mathrm{RT} \xrightarrow{-\beta^-} [\mathrm{RHe^+}] \rightarrow [\mathrm{R^+He}] \rightarrow \mathrm{R^+} + \mathrm{He} \quad .$$

The use of repeatedly tritiated starting compounds made it possible to obtain labelled charged molecular species, the chemical state of which may be followed from their radioactivity.

In the present review, an attempt is made to discuss the theoretical and experimental foundations of the method and also to examine systematically the experimental results published up to May, 1974.

II. THEORETICAL AND EXPERIMENTAL FOUNDATIONS OF THE APPLICATION OF β-DECOMPOSITION PROCESSES IN THE STUDY OF ION–MOLECULE REACTIONS

The possibility of employing β-decomposition processes in the study of ion–molecule reactions is based on a series of theoretical and experimental investigations of nuclear transformations of this type and their chemical consequences.

The first result of the β-transformation of a radioactive atom is known to be the formation of a singly charged atom of a neighbouring element in the Periodic Table (the daughter atom) in accordance with the following scheme:

$${}^{A}_{z}\mathrm{M}_{A-z} \rightarrow {}^{A}_{z+1}[\mathrm{D}]^{+}_{A-z-1} + e^- + \tilde{\nu} \ ,$$

where P and D are the symbols for the parent and daughter elements, A and z are the mass number and nuclear charge of the atom of the parent element, and e^- and $\tilde{\nu}$ are the β-particle and antineutrino respectively. For the β-decomposition of the tritium atom, this scheme assumes the following form: ${}^{3}_{1}\mathrm{H}_2 \rightarrow {}^{3}_{2}\mathrm{He}^{+}_{1} + e^{-1} + \tilde{\nu}$.

The subsequent fate of the $[\mathrm{D}]^+$ ion formed depends on a number of factors, which include in the first place the shaking effect. The shaking effect, i.e. the perturbation of the electron shells in consequence of the sudden change in nuclear charge, is one of the most important causes of excitation and additional ionisation of the singly charged ion of the daughter element. Calculations of the probabilities of the excitation and additional excitation of daughter atoms have shown[46,47] that a considerable proportion of these ions (up to 80%) are in the ground electronic states and that the overall yield of multiply charged ions does not exceed 20%, most of them consisting of ions having the +2 charge.

Similar calculations for the β-decomposition of isolated tritium atoms[48] showed that 70% of the decomposition steps lead to the formation of non-excited $\mathrm{He^+}$ daughter ions, 25% give rise to daughter ions in the first excited level (40.5 eV), 2.5% yield daughter ions in levels with energies between 40.5 and 54.4 eV, and only 2.5% lead to the formation of doubly charged $\mathrm{He^{2+}}$ daughter ions. A characteristic feature of the β-decomposition of tritium atoms is the impossibility of the formation of ions of the daughter element with a charge greater than +2. The highly charged states arising in the β-decomposition of the atoms of other elements can be produced as the result of the ionisation of the inner electron shells in consequence of the shaking effect and the subsequent cascades of vacancies. In the β-decomposition of tritium, the development of vacancy cascades is impossible owing to the presence of only one electron shell.

We have discussed hitherto processes leading to the excitation and ionisation of the daughter atom formed on β-decomposition of isolated tritium atoms. We shall now consider how these effects are manifested when the atom undergoing decomposition forms part of a molecule. The electronic processes developing in the atom as a result of β-decomposition take place over a period much shorter than the period of atomic vibrations; one can therefore assume that these processes, occurring in atoms, predetermine the set of energy and charge states of the molecular ions. Since the yield of non-excited $\mathrm{He^+}$ daughter ions formed in β-transformations of isolated tritium atoms is about 70%, one may expect approximately the same yield of non-excited primary molecular ions $[\mathrm{RHe}]^+$ in the β-decomposition of tritium atoms forming part of the molecules RT.

The primary molecular ions subsequently undergo a number of transformations, which include in the first place electronic transitions, accompanied by the migration of charge, from the helium atom to other atoms in the primary molecular ions:

$$\left[\overset{\overset{e^-}{\curvearrowright}}{\mathrm{RHe}^+}\right] \longrightarrow \left[\mathrm{R^+He}\right] \quad .$$

Such a charge distribution can be accounted for by the fact that the ionisation potential of the helium atom (24.581 eV) is much higher than the ionisation potential of organic radicals (< 10 eV).

The next process undergone by the species generated is their decomposition with formation of the ion $\mathrm{R^+}$ and a helium atom. Since the energy of the C–He bond is estimated as only 0.18 eV,[49] this decomposition should occur over a period close to the period of the atomic vibrations. Subsequent spatial separation of the species produced takes place owing to the momentum acquired by the helium atom as a result of radioactive recoil.

Radioactive recoil is due to the emission of a nuclear electron and an antineutrino. The maximum recoil energy is defined by the expression[50]

$$E_{\mathrm{max}} = 536 \cdot 10^{6} E^{\beta}_{\mathrm{max}} \left(\frac{E^{\beta}_{\mathrm{max}} + 1.02}{M_{\mathrm{D}}} \right) ,$$

where E_{max} is the maximum recoil energy (MeV), E^{β}_{max} the maximum energy of the β-particle (MeV), and M_{D} the mass of the daughter atom (a.m.u.).

Since the emission energy of tritium is minimal ($E^{\beta}_{\mathrm{max}} = 0.0186$ MeV) compared with the emission energies of other β-radioactive isotopes, the recoil energy in the decomposition of tritium is small. The maximum recoil energy calculated from the above formula is only 3.35 eV.

In the β-decomposition in atomic systems, the recoil energy is generated in the form of the kinetic energy of the daughter atoms. In the general case of β-decomposition of an atom in a molecular system, part of the recoil energy can be consumed in the dissociation of the bond between the daughter atom and the remainder of the molecule. This component is determined by the rotational-vibrational coefficient $(M - M_{\mathrm{D}})/M$, i.e. depends on the ratio of the mass of the residue $M - M_{\mathrm{D}}$ and the mass of the molecule M.[51] In the decomposition of tritium forming part of various organic molecules, the rotational-vibrational coefficient is close to unity and one can therefore expect that a considerable proportion of the recoil energy will be consumed in the excitation of the molecular ion as a whole. However, owing to the virtually zero energy of the C–He bond, the helium atom in the intermediate species $[R^+He]$ can be regarded as free and the entire recoil energy is therefore generated as the kinetic energy of the helium atoms.

Thus theoretical studies of the β-decomposition processes and the accompanying transformations lead to the following conclusion important for the problem under consideration: the main chemical consequence of the β-decomposition of tritium atoms forming part of the molecule RT is the formation of non-excited singly charged molecular ions R^+.

Among the systems investigated at the present time, only one instance is known in which the above rule does not hold. This applies to the simplest tritium-containing compound—tritiated hydrogen (R = H or T). The primary molecular ions $^3HeH^+$ and $^3HeT^+$, formed in the β-decomposition of tritium forming part of the TH and T_2 molecules respectively, are extremely stable charged molecular species. The high stability of the protonated and tritonated helium species is not surprising, since their isoelectronic analogue, the $^4HeH^+$ ion, has been detected in mass spectrometers as early as the 1920s. The latter ion, which is the simplest two-electron heteronuclear particle, has been the subject of numerous theoretical calculations. Its dissociation energy, calculated by a number of workers [52-65] using different methods, is in the range between 1.46 and 2.04 eV. A value of the dissociation energy of the HHe^+ ion close to the calculated results has been obtained in the photoionisation studies of Chupka and Russell [66].

According to Cantwell's calculation [67], the major proportion of the primary molecular ions formed in the β-decomposition of tritium in the T_2 molecule are in the ground state, 11% are in the first excited level, and 4.5% are in the second excited level. Schwartz [68] estimated the fraction of primary molecular ions in the ground state as 93%. Taking these data into account as well as all that has been said previously about the excitation energy acquired by the primary molecular ions in consequence of the shaking effect and radioactive recoil, one may conclude that, in the vast majority of these ions, energy sufficient for the dissociation of the HeH bond cannot be located in the latter. For this reason, the main result of the β-decomposition of tritium in the TH and T_2 molecules is the formation of the non-excited molecular ions $^3HeH^3$ and $^3HeT^+$.

Table 1. The relative yields of ionic fragments in the β-decomposition of TH.

Ion	Yield, %		Ion	Yield, %	
	according to Ref.69	according to Ref.70		according to Ref.69	according to Ref.70
$^3HeH^+$	93±1.9	89.5±1.1	H^+	1.55±0.16	2.3±0.4
$^3He^+$	5.1±0.3	8.2±1.0	$^3He^{2+}$	0.14±0.01	—

The results of theoretical studies on the chemical consequences of the β-decomposition of tritiated compounds have been confirmed in numerous experimental investigations. Among these, one can isolate two groups of studies which differ fundamentally as regards the methods used to investigate the consequences of β-transformations. One of these groups comprises investigations where the charged fragments arising on β-decomposition of the tritium incorporated in various molecules were studied by the mass-spectrometric technique [69-78]. The other group comprises investigations devoted to the study of the same problem by radiochemical methods [42,79].

Without considering in detail the methodological problems of mass-spectrometric studies, we may note that in all cases instruments were used which made it possible to analyse the ions formed directly on β-decomposition of gaseous tritium-containing compounds. Table 1 presents the results of two independent mass-spectrometric determinations of the yields of ionic fragments arising on β-decomposition of the TH molecule [69,70].

Despite certain differences between the instruments used in these studies, the results are in good agreement. The principal characteristic feature of the latter is the high yield of the $^3HeH^+$ molecular ions.

Table 2. The relative yields of ionic fragments in the β-decomposition of T_2.

Ion	Yield, %
T^3He^+	94.5±0.6
$T^+ + {}^3He$	5.5±0.6

Wexler [70] established that the primary molecular ion $^3HeT^+$ formed on β-decomposition of the T_2 molecule is still more stable (Table 2).

The yields of fragment ions formed on β-decomposition of tritium in the CH_3T, [71] C_2H_5T, [72] n- and iso-C_3H_7T, [73] C_6H_5T, [74] $C_6H_5CH_2T$, and *o*-, *m*-, and *p*-$CH_3C_6H_4T$ [73] molecules have also been determined by the mass-spectrometric technique. As predicted by theoretical studies, the principal charged molecular species in the above instances proved to be the corresponding carbonium ions R^+. The yields of these species are compiled in Table 3.

The radiochemical method for the investigation of the chemical consequences of tritium decomposition processes in certain hydrocarbons has been used by Italian investigators [42,79]. It is important to note that these studies were carried out at the usual pressures, where the fragments arising as a result of the decomposition of the primary molecular ions were able to interact with the molecules of the initial substances and certain additives. A conclusion concerning the nature of the processes involving the primary molecular ions was reached on the basis of the nature and yields of the products of these reactions. For example, it was established [42] that the β-decomposition of one of the tritium atoms in the CT_4 molecule in a mixture containing 84% C_3H_8, 14% CT_4, and 2% O_2 is accompanied by a change in the isotope composition of methane. Together with the initial CT_4 molecules, those of CT_3H appeared, the radioactivity of the latter amounting to 74% of the total radioactivity of the primary CT_3He^+ molecular ions generated during the experiments. The formation of the triply labelled methane can be accounted for by the exothermic hydride ion transfer reaction between the labelled methyl cation and propane:

$$CT_3^+ + C_3H_8 \rightarrow CT_3H + C_3H_7^+ \quad . \qquad (1)$$

Since CT_3H is the main product of the reaction and its formation can be accounted for only in terms of reaction (1), the authors [42] concluded that the principal result of the decomposition of tritium in methane is the formation of the methyl cations CT_3^+. It is noteworthy that in the case under consideration the initial mixture was at atmospheric pressure. The similarity of the results of the mass-spectrometric studies and the studies carried out by the Italian workers permits the conclusion that the yields of the charged fragments are independent of the pressure at which they are formed.

Table 3. The yields of carbonium ions in the β-decomposition of tritium forming part of hydrocarbons.

Initial cpd.	Carbonium ion	Yield, %	References	Initial cpd.	Carbonium ion	Yield, %	References
CH_3T	CH_3^+	83	71	$2\text{-}C_3H_7T$	$2\text{-}C_3H_7^+$	41	73
C_2H_5T	$C_2H_5^+$	80	72	C_6H_5T	$C_6H_5^+$	72	74
$1\text{-}C_3H_7T$	$1\text{-}C_3H_7^+$	56	73	C_7H_7T	$C_7H_7^+$	78	73

Thus it follows from the theoretical and experimental studies discussed above that the processes involving the β-decomposition of tritium in molecular systems lead to the formation of the corresponding molecular ions. These processes in fact constitute the basis of the radiochemical method for the investigation of ion–molecule reactions.

III. FOUNDATIONS OF THE EXPERIMENTAL TECHNIQUES IN THE RADIOCHEMICAL METHOD FOR THE INVESTIGATION OF ION-MOLECULE REACTIONS

In order to investigate the reactions of 1-propyl and 2-propyl cations, the ions must be generated from [1-T]propane in the former case:

$$CH_3CH_2CH_2T \xrightarrow{-\beta^-} CH_3CH_2CH_2^+ + He$$

and from [2-T]propane in the latter case:

$$CH_3CHTCH_3 \xrightarrow{-\beta^-} CH_3C^+HCH_3 + He \quad .$$

For ion–molecule reactions, such labelled compounds are then introduced into a medium containing the substances involved in the reaction of the propyl cations to be investigated and the resulting mixture is kept until the products of the ion–molecule interactions accumulate.

In order to identify the products formed on interaction of the small number of ions arising in the β-decomposition during a time interval suitable for the experiment and to determine their yields, it is necessary to employ polytritiated compounds[80], i.e. compounds containing at least two tritium atoms. In this case the β-decomposition of one of the radioactive atoms leads to the formation of a molecular ion and the presence of another tritium atom ("the label") in the ion makes it possible to investigate the products of the ion–molecule reactions. For example, in the case considered here one must employ [1-T_2]propane {or [1-T_3]propane} and [2-T_2]propane. The interaction of the labelled ion obtained as a result of the reactions

$$CH_3CH_2CT_3 \xrightarrow{-\beta^-} CH_3CH_2CT_2^+ + He \quad , \tag{2}$$

$$CH_3CT_2CH_3 \xrightarrow{-\beta^-} CH_3C^+TCH_3 + He \tag{3}$$

with the molecules of the surrounding medium leads to the formation of radioactive products. They are analysed by the usual methods employed for labelled compounds.

Thus the experimental method for the investigation of ion–molecule reactions initiated by the β-decomposition of tritiated compounds include three main stages:

1. the synthesis of a suitable polytritiated source of molecular ions;
2. the preparation of the reaction mixture and accumulation of the products of the ion–molecule reactions;
3. analysis of the reaction products.

1. Synthesis of the Initial Polytritiated Compound

The simplest and most readily available tritium-containing compound which may be used as the source of HeT^+ ions is molecular tritium, which is used by the isotope industry in large amounts and is very pure (up to 99%).

Other polytritiated compounds are not manufactured on an industrial scale and are synthesised under laboratory conditions. Such syntheses involve considerable experimental difficulties[81,82]. Several tens of syntheses of polylabelled compounds have now been described, most of the products being tritiated derivatives[83-89].

2. Preparation of the Reaction Mixture and Accumulation of the Products of the Ion–Molecule Reactions

By virtue of the characteristics of the nuclear-chemical processes mentioned above, the radiochemical method for the investigation of ion–molecule reactions permits the study of the interaction of molecular ions with both individual substances and with their mixtures in any state of aggregation. In the preparation of the reaction mixture, the choice of the optimum specific radioactivity is important. The use of a low specific activity of the mixture leads to an increase of the duration of the experiment. The accumulation of a sufficient amount of products for detection at a low specific activity requires a long exposure time. For example, the molecular ions CT_3^+ formed in one month as a result of the decomposition of tritium in CT_4 have an overall activity of only about 1% of the total activity of the source of these ions, i.e. CT_4.

On the other hand, the employment of a high specific activity involves the possibility of undesirable radiolytic processes, because, as a result of the β-decomposition, the reaction system is exposed not only to molecular ions but also to β-particles with an average energy of 5.6 keV. The latter can decompose a definite fraction of the initial tritiated compound, which leads to the formation of labelled products indistinguishable from the products of the ion-molecule reactions investigated. In order to prevent these secondary processes, it is necessary to prepare reaction mixtures with a fairly low level of specific activity. Calculations based on the G factors and estimates of the dose received by the system have shown, for example, that the rate of formation of tritiated radiolysis products in alkanes is negligibly small for a specific activity less than 0.5 mc $mmole^{-1}$ [42].

This conclusion was confirmed experimentally by the so called "blank" experiments involving the employment of singly labelled compounds with the same specific activity as the corresponding polylabelled compounds[42,79]. Since the decomposition of monotritiated molecules leads to the formation of ions without a radioactive label, the detection in such experiments of any tritiated products different from the initial compound indicates the occurrence of radiolytic processes. "Blank" experiments carried out for a number of systems have shown that the radiation-induced decomposition of the specimens is not a significant source of tritiated products if the system has a specific activity less than 0.5 mc mmole^{-1}.

In order to suppress the radiolytic processes, suitable diluents are added to the specimens until the attainment of the required specific activity. Italian investigators[42,79] used for this purpose suitable carriers, while the experiments carried out at Leningrad University[140-146] involved the employment of noble gases (argon or xenon). In contrast to carriers, the inert gases suppress radiolytic processes but do not take part in the reactions with the molecular ions formed and do not therefore complicate the ion–molecule interactions investigated.

The mixture of the initial polytritiated compound and the substrate, diluted until the attainment of a specific activity of several tenths of mc mmole^{-1}, is sealed in tubes with a volume of several milli-metres and is maintained until the accumulation of the products of the ion–molecule reactions. The accumulation time, which depends on the specific activity of the mixture and the sensitivity of the analytical method, varies from several days to several months.

3. Analysis of the Products of the Ion–Molecule Reactions

The relatively low radioactivity of the molecular ions formed during the experiment and consequently the low radioactivity of the products of their interaction as well as the fact that the latter are always analysed in the presence of a large amount of the undecomposed polytritiated starting compound necessitates the employment of a sensitive and effective analytical technique. The most convenient methods for the qualitative and quantitative analysis of the labelled products of ion–molecule interactions are chromatographic procedures and particularly the gas radiochromatographic method‡.

Apart from the qualitative and quantitative analyses of the products, the determination of the intermolecular distribution of tritium in such products is extremely interesting. The available information about the intramolecular distribution of the label throws light on the mechanisms of the processes leading to the formation of such products. The study of the distribution of tritium within the molecule is usually based on the change of the specific activity of the compound when a hydrogen atom in a given position (or a whole group of atoms) is substituted by a suitable inactive group. Such analysis has been carried out, for example, in the study of the products of the interaction of HeT$^+$ ions with toluene[95,96].

It is noteworthy that, in order to investigate the processes involving the neutralisation of the molecular ions formed on β-decomposition of tritiated compounds, the method proposed by Lloyd and coworkers[97,98] is extremely promising. In this method, the products of the neutralisation of the molecular ions (radicals) are investigated by electron spin resonance.

IV. ION–MOLECULE REACTIONS INITIATED BY THE β-DECOMPOSITION OF MOLECULAR TRITIUM

As already mentioned, the β-decomposition processes involving molecular tritium can be used to generate ionised molecules of tritiated helium (HeT$^+$) and to investigate a wide variety of reactions of these species.

The possibility of ion–molecule reactions with participation of HeT$^+$ ions was first reported by Wilzbach[99]. Subsequently this study constituted the basis of a new and extremely promising method for synthesising tritiated compounds, which has now been called the "Wilzbach method": a mixture of organic substances is prepared with an amount of gaseous tritium such that the radioactivity of the mixture is equal to several curies and the system is allowed to stand for several days. The nuclear-chemical processes developing in the system lead to the formation of a wide variety of labelled compounds.

The bulk of the studies employing this method involved its preparative aspect. However, there have been several investigations whose subject was the mechanisms of the formation of tritiated compounds. For example, Yang and Gant carried out a series of studies[100-103] designed to elucidate the role of various pathways to the formation of tritiated products from ethane, ethylene, cyclopropane, and propane containing gaseous tritium. The principal conclusion derived from these investigations is that labelled compounds are formed via two types of reaction: the reactions initiated by HeT$^+$ ions and the reactions initiated by β-particles.

In conformity with the point of view adopted at the present time[104], the formation of labelled compounds by the Wilzbach method involves mainly radiation processes. For this reason, studies on the introduction of a label into organic compounds by the Wilzbach method yield only limited information about the reaction of HeT$^+$ ions. On the other hand, the radiochemical method for the investigation of ion–molecule reactions examined here is free from this disadvantage.

1. The Reactions of HeT$^+$ Ions with Alkanes and Cycloalkanes

The reactions of the molecular ions HeT$^+$, formed on β-decomposition of molecular tritium, with methane, ethane, propane, butane, and isobutane as well as cycloalkanes ranging from C_3 to C_6 have been the subject of detailed studies by a group of workers at Rome University[105-107]. Tables 4 and 5 list the yields of the labelled products of the interaction of HeT$^+$ ions with alkanes and cycloalkanes respectively.

Table 4. The products of the interaction of HeT$^+$ ions with alkanes.

Alkane	Yields of products, %						Overall yield
	CH_3T	C_2H_5T	C_2H_3T	C_3H_7T	n-C_4H_9T	iso-C_5H_9T	
CH_4	40	2	13	—	—	—	55
C_2H_6	14	34	—	—	—	—	48
C_3H_8	12.8	5.1	—	12.3	—	—	30.2
n-C_4H_{10}	15.2	6.2	2.5	2.3	15.3	—	41.5
iso-C_4H_{10}	23.4	1.7	3.5	3.2	—	17.9	49.7

The following main conclusions can be drawn from the tabulated results: (a) the overall yield of the tritiated hydrocarbons is relatively low (from 25 to 55%); the

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‡ In order to become acquainted with the method of gas radiochromatography, the reader may be recommended to consult Refs. 90–94.

authors suggest that the remaining activity corresponds to HT §; (b) in all the systems investigated, the labelled initial hydrocarbon is formed in a high yield; (c) the reactions of HeT^+ ions with alkanes are not accompanied by isomerisation processes; (d) when HeT^+ ions react with cycloalkanes, high yields of the corresponding labelled cyclic hydrocarbons are formed, which indicates the retention of the cyclic structure of the intermediate species.

Table 5. The products of the interaction of HeT^+ ions with cycloalkanes.

Cycloalkane	Yields of products, %						
	HT	CH_3T	C_2H_5T	C_2H_3T	C_3H_7T	C_3H_5T	initial [T] cycloalkane
Cyclopropane	~35	23.0	3.7	12.1	2.2	6.7	19.2
Cyclobutane	~45	1.3	6.1	11.1	—	8.4	6.9
Cyclopentane	~65	—	2.6	4.1	4.6	3.4	11.1
Cyclohexane	75	—	1.2	1.6	2.7	3.0	9.7

In their discussion of the results of studies on the reactions of HeT^+ ions with alkanes, Cacace and coworkers[105,106] assumed that the first stage in these reactions is the protonation (or more precisely tritonation) of the initial hydrocarbons in accordance with the following general mechanism:

$$C_nH_{2n+2} + HeT^+ \rightarrow [C_nH_{2n+2}T]^+ + He \quad . \qquad (4)$$

Reaction (4) is analogous to the gas-phase protonation of the simplest hydrocarbons, for example methane by H_3^+, D_3^+, CHO^+, CH_5^+, and CH_4^+ ions[108-117], ethane by CH_5^+, H_3^+, D_3^+, and CHO^+ ions[108,111,115], and deuteriated propane by CH_5^+ ions[118], which is well known in mass spectrometry.

The $[C_nH_{2n+2}T]^+$ carbonium ions formed as a result of reaction (4) are in an excited state and their excitation energy increases with increase of n. Some of these excited molecular ions are stabilised on collisions with the molecules of the surrounding medium:

$$[C_nH_{2n+2}T]^+_{exc} + S \rightarrow [C_nH_{2n+2}T]^+ + S_{exc} \qquad (5)$$

while some undergo monomolecular decomposition via various energetically allowed pathways, the most probable and general of which for all the systems investigated are the following fragmentation reactions:

$$[C_nH_{2n+2}T]^+_{exc} \begin{cases} \nearrow [C_nH_{2n+1}]^+ + HT & (6a) \\ \searrow [C_nH_{2n}T]^+ + H_2 \quad . & (6b) \end{cases}$$

The stabilised tritonated hydrocarbons then undergo neutral thermal reactions with the inactive substrate molecules, involving proton transfer and reforming the initial labelled hydrocarbons¶:

$$[C_nH_{2n+2}T]^+ + C_nH_{2n+2} \rightarrow C_nH_{2n+1}T + [C_nH_{2n+3}]^+ \quad . \qquad (7)$$

Thus the consecutive processes (4), (5), and (7) explain the formation of the labelled initial compound—one of the principal products of the reactions of HeT^+ ions with alkanes, while the decrease of the stability of the $[C_nH_{2n+2}T]^+$ carbonium ions with increase of the number of carbon atoms explains the decrease of the yield of the corresponding tritiated hydrocarbons on passing from methane to butane.

As already mentioned, one of the characteristics of the reactions of HeT^+ ions with alkanes is the comparatively low overall yield of tritiated hydrocarbons. Although Cacace and coworkers did not determine the yield of hydrogen tritide, one can be certain that the remaining fraction of radioactivity corresponds to this compound. This hypothesis is supported by the high yield of HT in the reactions of HeT^+ ions with cycloalkanes (Table 5).

According to the general mechanisms of the first stages of the ionic processes quoted above, the formation of labelled hydrogen can be accounted for by the fragmentation of a considerable proportion of the excited $[C_nH_{2n+2}T]^+$ carbonium ions via reaction (6a). However, if it is supposed that all the hydrogen atoms in the excited tritiated hydrocarbon are equivalent, then, as a result of the statistical distribution of tritium atoms, the ratio of the activity of hydrogen (A_{HT}) and that of the corresponding carbonium cation ($A_{C_nH_{2n}T^+}$) is $2/(2n + 1)$ and this in turn implies that the overall yield of the tritiated hydrocarbons, formed mainly in the successive interactions of the $[C_nH_{2n}T]^+$ carbonium ions, should be much higher than the yield of HT. For example, in the interaction between HeT^+ and butane about 80% of the radioactivity should pass to the hydrocarbons. Similar considerations have served as a basis for the hypothesis that the HeT^+ molecular ions not only manifest powerful protonating properties but also the properties of Lewis acids, i.e. these species are capable of abstracting a hydride ion from hydrocarbons, forming HT as the single tritium-containing product:

$$C_nH_{2n+2} + HeT^+ \rightarrow C_nH^+_{2n+1} + HT + He \quad .$$

This hypothesis explains the low yield of labelled hydrocarbons.

The present authors believe that, while attributing to the HeT^+ ions the properties of Lewis acids in the reaction of these species with alkanes ranging from C_2 to C_4, Cacace and coworkers[105,106] unjustifiably failed to mention the possibility of reactions involving the abstraction of a hydride ion in the T_2–CH_4 system. Indeed, if HeT^+ reacted solely as a Brønsted acid via reactions (4)–(7), the yield of labelled hydrocarbons should be much higher than that obtained by the authors. According to Aquilanti and Volpi[111], about 50% of the methyl carbonium ions should be stabilised and should then give rise to tritiated methane via reaction (7). The remaining 50% of ions decompose via reaction (6), forming 20% HT and 30% CH_3T in accordance with the formula quoted above. Thus the overall radioactivity of the hydrocarbons should be 80%, which is much higher than the experimental value.

The formation of the remaining products of the interaction of HeT^+ ions with alkanes can be explained by the subsequent reactions of the $[C_nH_{2n}T]^+$ carbonium ions formed via reaction (6b) with substrate molecules and also via other pathways involving the fragmentation of the excited $[C_nH_{2n+2}T]^+$ carbonium ions. For example, it has been suggested[106] that CH_3T, found in high yields in all the systems investigated, is formed as a result of the following monomolecular decomposition of tritonated hydrocarbons:

$$[C_nH_{2n+2}T]^+_{exc} \rightarrow [C_{n-1}H_{2n-1}]^+ + CH_3T \quad . \qquad (8)$$

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§ Unfortunately the authors of the studies quoted here did not carry out an analysis for hydrogen tritide in the reactions between HeT^+ ions and alkanes.

¶ Similar reactions are well known in mass spectrometry[111].

The results of studies on the reactions of HeT⁺ ions with cycloalkanes can be explained similarly (Table 5). It is interesting to note that, with increase of the molecular weight of the initial cyclic hydrocarbons, the yield of HT rises from 35% for cyclopropane to 75% for cyclohexane. The authors explain this behaviour by the fact that, when there is competition between triton transfer

$$\text{cyclo-}C_nH_{2n} + HeT^+ \rightarrow [C_nH_{2n}T]^+_{exc} + He \qquad (9)$$

and the abstraction of a hydride ion

$$\text{cyclo-}C_nH_{2n} + HeT^+ \rightarrow [\text{cyclo-}C_nH_{2n-1}]^+ + HT + He \qquad (10)$$

reaction (10) becomes dominant on passing from cyclopropane to cyclohexane.

The detection of labelled cyclic hydrocarbons among the products of the ion–molecule interactions shows that the carbonium ions formed by reaction (9) also have a cyclic structure. These results constitute direct proof of the formation of gas-phase cycloalkyl carbonium ions, the existence of which has been postulated for a long time but has not been demonstrated experimentally†.

2. The Reactions of HeT⁺ Ions with Aromatic Hydrocarbons

The gas-phase ion–molecule reaction initiated by the β-decomposition of T_2 in aromatic hydrocarbons (toluene, anisole, fluoro-, chloro-, and bromo-benzenes, and $\alpha\alpha\alpha$-trifluorotoluene) have been reported[121–124]. We shall begin the discussion of these results from three standpoints: the mechanisms of the formation of the products, the intramolecular distribution of tritium in the products, and the relative reactivities of the aromatic compounds.

Table 6. The products of the interaction of HeT⁺ ions with aromatic compounds.

Aromatic cpd.	Yields of products, %		
	initial [T] cpd.	[T] benzene	other products
$C_6H_5CH_3$	60±8	3.8±0.5	[T] methane (about 8%)
$C_6D_5CD_3$	60±8	3.6±0.5	[T] methane (about 6%)
$C_6H_5C_4H_9$	65±10	25±4	[T] toluene (0.9 ± 0.1%), [T] ethylbenzene, and [T] xylenes (3.6 ± 0.4%)
$C_6H_5OCH_3$	49±10	2.0±0.2	—
C_6H_5F	67±10	<0.2	—
C_6H_5Cl	76±10	3.7±0.8	—
C_6H_5Br	69±10	8±1	—
$C_6H_5CF_3$	81±10	2.9±0.3	—

Table 6 presents the yields of the identified products of the reactions considered. Evidently the main products in all the systems investigated are the labelled initial compounds and benzene, the overall yield of the tritium-containing hydrocarbons being much higher than in reactions of HeT⁺ ions with alkanes and cycloalkanes. These data led to the hypothesis that the higher stability of the protonated arenes, formed via the extremely exothermic (–100 kcal mole⁻¹) reaction

$$ArX + HeT^+ \rightarrow [ArXT]^+_{exc} + He \qquad (11)$$

enables a considerable proportion of these ions to become stabilised on collision with the molecules of the aromatic hydrocarbon ArX (X = CH_3, C_4H_9, OCH_3, F, Cl, Br, or CF_3). The stabilised tritiated ion then transfers a proton to the substrate molecule in accordance with the neutral thermal reaction

$$[ArXT]^+ + ArX \rightarrow \overline{ArX} + [ArXH]^+ \quad , \qquad (12)$$

where $\overline{ArX}$ denotes a labelled compound.

Thus reactions (11) and (12) lead to the formation of the main products of the reactions investigated—the tritiated initial aromatic hydrocarbons.

Some of the excited tritonated molecules which have not been stabilised undergo monomolecular fragmentation:

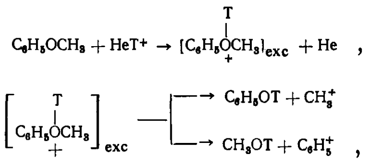
$$[ArXT]^+_{exc} \rightarrow ArT + X^+ \quad .$$

As already mentioned, the overall radioactivity of the products identified was lower than the radioactivity of the HeT⁺ ions generated during the experiment. Cacace and coworkers do not explain this radioactivity deficit in most instances[121,122] and sometimes[123] assume that part of the radioactivity is lost on the walls of the reaction vessel or is contained in products, undetected under the given conditions of analysis, which are formed in the reaction between HeT⁺ and nucleophilic impurities present in the reaction mixture in trace amounts. We believe that a more logical and more consistent hypothesis, in the light of previous investigations, would be that, as in the reactions with alkanes and cycloalkanes, in the reactions considered here HeT⁺ ions possess not only protonating properties but also the properties of Lewis acids, i.e. they react with aromatic compounds as follows:

$$C_6H_5X + HeT^+ \rightarrow C_6H_4X^+ + HT + He$$

forming HT, whose yield was not unfortunately determined.

Furthermore, there is no doubt that in the reactions with aromatic compounds having substituents with lone electron pairs ($C_6H_5OCH_3$, C_6H_5Cl, C_6H_5Br, C_6H_5F), some of the HeT⁺ ions interact with the electron pairs, forming the corresponding oxonium and halogenonium ions. The monomolecular fragmentation of subsequent bimolecular reactions of these ions lead to the formation of labelled alcohols or hydrogen halides. For example, the reactions



$$C_6H_5OCH_3 + HeT^+ \rightarrow [C_6H_5\overset{T}{\underset{+}{O}}CH_3]_{exc} + He \quad ,$$

$$\left[C_6H_5\overset{T}{\underset{+}{O}}CH_3\right]_{exc} \rightarrow \begin{cases} C_6H_5OT + CH_3^+ \\ CH_3OT + C_6H_5^+ \end{cases} ,$$

which compete with those determined previously, can account for the relatively low yield (51%) of labelled products found by Cacace et al.[123] It is regrettable that the authors did not attempt to detect among the reaction products labelled compounds formed as a result of the electrophilic attack by HeT⁺ ions on the heteroatoms of the substituents.

Extremely important information about the ion–molecule processes developing in the system and about the nature of the intermediate protonated arenes may be obtained by studying the intramolecular distribution of tritium in the final reaction products. Here one can assume that the distribution of the label in the final products reflects the selectivity of the initial interactions of the HeT⁺ ions with various positions of the reacting molecule.

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†There have been numerous reports of the formation of such ions in solution[119,120].

The intramolecular distribution of tritium in the products of the reaction of HeT^+ ions with toluene, anisole, $\alpha\alpha\alpha$-trifluorotoluene, and halogenobenzenes has been investigated[121-124]. The results of these studies, illustrated in Fig. 1, lead to the following general conclusion. In their gas-phase interaction with the π electrons of the aromatic ring, HeT^+ ions exhibit an appreciable selectivity, although the latter is not high. The fact that the selectivity of the protonation reaction is low is satisfactorily consistent with the general rule familiar for electrophilic substitution in solutions, according to which an increase of the reactivity of the electrophilic species entails a decrease of the positional selectivity[125]. Among the known Brønsted acids, the gaseous non-solvated HeT^+ ion is one of the most reactive species. It is therefore not surprising that it exhibits a low selectivity in the reactions investigated.

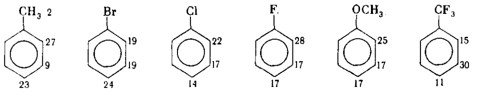

Figure 1. The intramolecular distribution of tritium in the products of the interaction of HeT^+ ions with aromatic hydrocarbons. The numerals denote the relative proportions of radioactivity (%) belonging to each position.

Table 7 presents data obtained in a study of the selectivity of aromatic compounds in reactions of HeT^+ ions (competing reactions). These data show that the reactivity of all the substances investigated, with the exception of $\alpha\alpha\alpha$-trifluorotoluene, in relation to HeT^+ ions is higher than the reactivity of benzene. One should note that the reactivity of aromatic compounds in reactions with HeT^+ ions is low. These results can also be explained by the high electrophilic reactivity of tritonated helium.

Table 7. The relative reactivities of aromatic compounds in the reaction with HeT^+ ions.

Aromatic cpd.	Reactivity in relation to benzene
ααα-Trifluorotoluene	0.8
Benzene	1.0
Fluorobenzene	1.2
Toluene	1.5
Chlorobenzene	1.6
Bromobenzene	2.0
Benzonitrile	2.2
Anisole	3.0

The results of studies on the reactions of the close analogue of tritonated helium, namely the D_2T^+ ion, with gaseous aromatic hydrocarbons (at a pressure of 750 mmHg and room temperature) are in good agreement with the results of the studies discussed above[126,127].

In conclusion of this section, we may note that the β-decomposition of molecular tritium in systems containing noble gases (Y) makes it possible to investigate the reactions of the tritiated ions YT^+ of the noble gases[128]. The radiochemical method for the generation of the tritiated ions of noble gases is based on the exothermic reaction

$$HeT^+ + Y \rightarrow He + YT^+ .$$

The only study on these lines was devoted to the investigation of the reactions of NeT^+ and XeT^+ ions with methane[128]. It was established that these reactions are analogous to those of HeT^+ ions with methane discussed previously.

The further employment of the radiochemical method for the study of the reactions of protonated noble gases will undoubtedly supplement the available information obtained in mass-spectrometric[129-134], radiation[135], and theoretical[65] studies on these interesting, reactive species.

V. ION-MOLECULE REACTIONS INITIATED BY THE β-DECOMPOSITION OF TRITIATED HYDROCARBONS

1. Reactions of Carbonium Ions with Alkanes and Cycloalkanes

Most of the studies on the reactions of carbonium ions generated in the β-decomposition of tritiated hydrocarbons are concerned with the bimolecular interaction of these species with non-radioactive sources of the corresponding ions. For example, studies have been made on the reactions of methyl cations with methane[42], of ethyl cations with methane[45,79], of propyl cations with propane[86], and of cyclopentyl cations with cyclopentane[87]. The results of these investigations are presented in Tables 8-11.

Table 8. The products of the interaction of methyl cations CT_3^+ with methane.

Product	Yield, %
CHT_3	<5.0
HT	28.7
Ethylene	10.9
Ethane	1.0
Propane	0.8
Propene	<0.02
n-Butane	0.3

Table 9. The products of the interaction of ethyl cations $C_2H_4T^+$ with ethane.

Product	Yield, %
Hydrogen	11.6±0.10
Methane	3.0±0.10
Ethylene	5.5±0.03
Propane	1.6±0.50
Butane	2.7±0.20
Propene	—

It is noteworthy that the experimental technique used in these investigations did not enable the authors to determine the yields of the products of the very important reaction involving the abstraction of an H^- ion from the reacting molecules by carbonium ions (with the exception of the methyl cation). Such hydride ion transfer reactions result in the formation of the molecules of the initial hydrocarbons but with one tritium atom less. For example, processes of this kind developing in the $C_2H_4T_2$–C_2H_6 system,

$$C_2H_4T_2 \xrightarrow{-\beta^-} C_2H_4T^+ + He \quad , \tag{13}$$

$$C_2H_4T^+ + C_2H_6 \rightarrow C_2H_5T + C_2H_5^+ \quad , \tag{14}$$

lead to the formation of monotritiated ethane, the yield of which cannot be determined against the background of the large amount of the initial doubly tritiated ethane‡. However, despite the fact that direct experimental proof of the occurrence of processes analogous to reactions (13) and (14) has not been obtained for the ethyl, propyl and cyclopentyl cations, the low yield of the identified products (ranging from 23 to 7%) suggests that such processes play a significant role.

Table 10. The products of the interaction of propyl cations $C_3H_6T^+$ with propane.

Product	Yield, %
Hydrogen	9.3
Methane	7.9
Ethane	1.9
Ethylene	4.9
Acetylene	0.7
Propane	6.0
Methylacetylene + allene	~4.9

Table 11. The products of the interaction of cyclopentyl cations $C_5H_8T^+$ with cyclopentane.

Products	Yield, %
Methane	1.6
Ethane	0.4
Propane	0.5
Butane	0.7
Pentene	3.5

Making this assumption and taking into account the decrease of the yield of the detected tritiated products with increase of the molecular weight of the ion, one may conclude that the transfer of a hydride ion from the hydrocarbon molecule to the carbonium ion is more characteristic of heavy ions. There have been numerous mass-spectrometric studies in which it has been shown that the hydride ion transfer reaction is characteristic of all the lower alkanes[113,115,116,138].

Another characteristic reaction of carbonium ions is known to be the condensation reaction[139]

$$[C_nH_{2n+1}]^+ + C_nH_{2n+2} \rightarrow [C_{2n}H_{4n+1}]^+ + H_2 \quad .$$

Such reactions lead to the formation of new carbonium ions. Their subsequent involvement in the hydride ion transfer reaction is responsible for the formation of heavier hydrocarbons. Thus condensation of the methyl cation and methane leads to the formation of a labelled ethyl cation. The latter does not react with methane, but, in the presence of even a small amount of propane, it is rapidly involved in the hydride ion abstraction reaction, forming labelled ethane (Table 8). It is also possible that similar processes take place in the $C_2H_4T_2$–C_2H_6 system. In this case the condensation reactions give rise to labelled butane.

Having examined the two main types of reactions of carbonium ions generated by the β-decomposition of tritiated hydrocarbons (with alkanes and cycloalkanes), we shall not discuss in detail the mechanism of the processes involving the formation of all the remaining products detected and we shall only note that the secondary ions produced by the fragmentation of the excited primary molecular ions are involved in such processes. A more detailed discussion of this problem can be found in the original papers quoted previously.

Table 12. The products of the interaction of methyl cations CT_3^+ with benzene and toluene.

Aromatic hydrocarbon	Yields of products, %				
	benzene	toluene	*p*-xylene	*m*-xylene	*o*-xylene
Benzene	52±3	48±3	—	—	—
Toluene	7±1	24±2	14±2	39±2	17±2

Table 13. The products of the interaction of methyl cations CT_3^+ with isomeric xylenes.

Substrate	Yields of products, %					
	p-xylene	*m*-xylene	*o*-xylene	mesitylene	pseudocumene	hemimellitene
p-Xylene	31±2	—	—	13±1	49±1	7±1
m-Xylene	—	42±2	—	20±1	26±2	12±2
o-Xylene	—	—	49±3	16±1	24±3	11±1

2. The Reactions of Carbonium Ions with Aromatic Compounds

The radiochemical method for the investigation of ion–molecule reactions has been used to investigate the gas-phase interactions of free methyl cations with benzene, toluene, and *m*-, *o*-, and *p*-xylenes[140] and also of the liquid-phase reactions of phenyl cations with benzene[89]. Tables 12 and 13, which list the relative yields of the labelled products of the interaction of methyl cations with benzene, toluene, and the isomeric xylenes, show that tritiated aromatic hydrocarbons having the same structures as the initial compounds as well as the products of the methylation of the latter are mainly formed.

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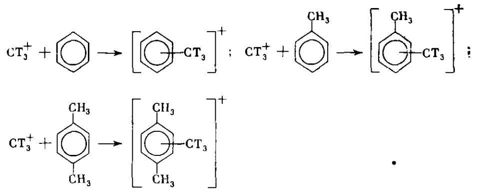
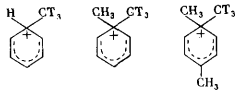
‡ A gas-chromatographic method of isotope analysis is available only for methane[136,137].

When methyl cations interact with aromatic hydrocarbons, the free *p*-orbital of the carbonium atom overlaps with the π orbitals of the aromatic ring, which results in the formation of the corresponding π complexes:

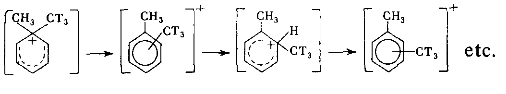


Such π complexes are known to be capable of isomerising to σ structures of the type



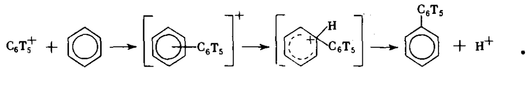
The further reactions of these σ complexes can proceed via two mechanisms. The first involves unimolecular decomposition with reformation of the molecules of the initial compounds§. The formation of labelled substrates by this mechanism is demonstrated by the discovery of labelled xylenes having the same structure as the initial compounds among the products of the interaction of methyl cations with xylenes.

The second mechanism of the reaction of the intermediate σ complexes involves their deprotonation. The deprotonation processes lead to the formation of labelled products of the methylation of the initial aromatic compounds. It is interesting to note that, as a result of such processes, labelled *m*-xylene is formed in the CT_4–toluene system in a yield exceeding those of *o*- and *p*-xylenes. These results are inconsistent with the familiar directing rule for electrophilic substitution reactions in solution. This discrepancy can probably be accounted for by a rearrangement in the corresponding phenonium ions¶:



The monomolecular deprotonation reactions of the intermediate phenonium ions are endothermic ($\Delta Q \simeq 100$ kcal mole^{-1}) and therefore occur only on collisions between ions and molecules capable of combining with a proton (in the present case toluene molecules are species of this kind). The interval between the collisions of the species in the reaction system is about 10^{-9} s. The time of the rearrangements is probably close to the period of the atomic vibrations (10^{-13} s). Thus rearrangements associated with the migration of methyl groups can occur several times before the phenonium ion loses a proton in a bimolecular collision with the surrounding molecules. The rearrangements of phenonium ions are proved convincingly by the results of experiments designed to investigate the interaction of methyl cations with xylene isomers. Regardless of the isomers used as the starting material, all three possible trimethylbenzene isomers were formed.

The study of the reactions of phenyl cations, generated in the β-decomposition of tritium in fully tritiated benzene, with non-radioactive benzene molecules showed that the only product of such reactions is labelled biphenyl[89]. Its formation can be accounted for by the same processes as in the formation of the methylation products in the reactions of methyl cations with aromatic compounds. These processes can be represented schematically as follows:



Together with labelled biphenyl, [T_5] benzene can also be formed. This product may be obtained via the reaction involving the abstraction of hydride ions, which is well known for carbonium ions:

$$C_6T_5^+ + C_6H_6 \rightarrow C_6T_5H + C_6H_5^+ \quad .$$

Unfortunately the method used in the above investigation[89] to analyse the products did not allow the isotope analysis of the tritiated benzene molecules.

3. The Reactions of Carbonium Ions with Compounds Containing Atoms having Lone Electron Pairs

In order to investigate this group of ion–molecule reactions, the starting materials used were inorganic and organic oxygen (water, alcohols, and ethers)[44,142-144], halogen (hydrogen and ethyl halides)[145], and nitrogen (amines)[146] compounds.

(a) **Reactions of carbonium ions with oxygen compounds.** Tables 14 and 15 present the results of the analysis of the products of the interaction of methyl cations with water, alcohols, and ethers. Evidently the main product of the interaction of methyl cations with water and alcohols is tritiated methanol and the products of the interaction of methyl cations with ethers are the corresponding labelled methyl-containing ethers.

Table 14. The products of the interaction of methyl cations CT_3^+ with water and alcohols.

Starting material	Yields, %					
	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$
H_2O	11±1	89±1	—	—	—	—
CH_3OH	4±1	86±2	10±1	—	—	—
C_2H_5OH	2±1	80±2	—	18±1	—	—
n-C_3H_7OH	—	85±2	—	—	15±1	—
iso-C_3H_7OH	—	100	—	—	—	—
n-C_4H_9OH	—	94±1	—	—	—	6±1
s-C_4H_9OH	—	100	—	—	—	—
iso-C_4H_9OH	—	100	—	—	—	—

To facilitate the consideration of these results, the initial oxygen-containing substances will be designated by ROR_X (where R and R_X = H or organic group). By virtue of the electrophilic nature of carbonium ions, the most characteristic processes in the interaction of methyl cations with compounds of the type considered involve the addition of these species to atoms with lone electron pairs

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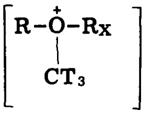
§The high yield of tritiated benzene in the CT_4–C_6H_6 system is probably associated with the isotope exchange between the tritium and protium atoms in the intermediate phenonium ions.

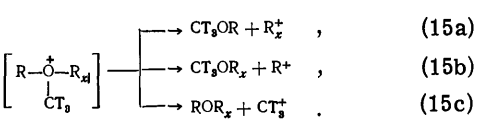
¶Such processes occur, for example, in the isomerisation of xylenes in the presence of acid catalysts[141].

(in the present instance oxygen atoms). Such addition results in the formation of excited† oxonium ions:



$$\left[R-\overset{+}{O}(CT_3)-R_X \right] .$$

Such ionium ions are known to exist in both gas and liquid phases[111,113,147]. Since the collision frequency of the species at atmospheric pressure is lower by 2–3 orders of magnitude than the bond vibration frequency, sufficient time elapses before the collision of the oxonium ion formed with any other species for the redistribution of the excitation energy throughout the ion. If part of the energy localised at the O–organic group bond exceeds the activation energy for the decomposition of the oxonium ion at this bond, the latter is ruptured under these conditions. The possible modes of fragmentation of the oxonium ion are represented below:



$$\left[R-\overset{+}{O}(CT_3)-R_x \right] \rightarrow CT_3OR + R_x^+ \quad , \qquad (15a)$$

$$\rightarrow CT_3OR_x + R^+ \quad , \qquad (15b)$$

$$\rightarrow ROR_x + CT_3^+ \quad . \qquad (15c)$$

Table 15. The products of the interaction of methyl cations CT_3^+ with ethers.

Initial ether ROR_X	Products	Q*, %	$Q_{ROCT_3}/Q_{ROCT_3} + Q_{R_xOCT_3}$	I_{R_x}**, eV
CH_3OCH_3	CT_3OCH_3	100	0.50	9.86
$CH_3OC_2H_5$	CT_3OCH_3	74±4	0.74	8.8
	$CT_3OC_2H_5$	26±3	—	—
$CH_3OC_3H_7$	CT_3OCH_3	90±3	0.90	8.69
	$CT_3OC_3H_7$	10±3	—	—
$CH_3OC_3H_7$-iso	CT_3OCH_3	91±2	0.91	7.9
	$CT_3OC_3H_7$-iso	9±2	—	—
$CH_3OC_4H_9$	CT_3OCH_3	90±4	0.90	8.64
	$CT_3OC_4H_9$	10±4	—	—
$CH_3OC_4H_9$-t	CT_3OCH_3	91±5	0.91	7.42
	$CT_3OC_4H_9$-t	9±4	—	—
$CH_3O(CH_2)OH$	CT_3OCH_3	19±1	0.50	7.0
	$CT_3O(CH_2)OH$	1	—	—
	CT_3OH	79±1	—	—
$CH_3OC_6H_5$	CT_3OCH_3	44±2	0.55	9.4
	$CT_3OC_6H_5$	36±1	—	—
	$CT_3C_6H_5$	1	—	—
	$CT_3C_6H_4OCH_3$	20±4	—	—
$CH_3OCH_2C_6H_5$	CT_3OCH_3	51±4	0.88	7.73
	$CT_3OCH_2C_6H_5$	7±1	—	—
	$CT_3C_6H_5$	26±5	—	—
	$CT_3C_6H_4CH_2OCH_3$	15	—	—
$C_2H_5OCH_3$	$CT_3OC_2H_5$	26±3	0.26	9.86
	CT_3OCH_3	74±4	—	—
$C_2H_5OC_2H_5$	$CT_3OC_2H_5$	100	0.50	8.8
$C_2H_5OC_3H_7$	$CT_3OC_2H_5$	72±2	0.72	8.69
	$CT_3OC_3H_7$	28±2	—	—
$C_2H_5OCH_2C_6H_5$	$CT_3OC_2H_5$	61±3	0.95	7.73
	$CT_3OCH_2C_6H_5$	3±1	—	—
	$CT_3C_6H_5$	22±4	—	—
	$CT_3C_6H_4CH_2OC_2H_5$	14±4	—	—
$C_3H_7OC_3H_7$	$CT_3OC_3H_7$	100	0.5	9.4
$C_3H_7OC_4H_9$	$CT_3OC_3H_7$	54±3	0.54	8.64
	$CT_3OC_4H_9$	46±3	—	—

* Q is the yield of reaction products.
** I is the ionisation potential.

One of the most important factors on which the probability of the decomposition of the ion via a particular channel depends is the stability of the products formed and in the first place the stability of the charged fragments[149]. It follows from Eqn. (15) that such charged fragments are the carbonium ions CT_3^+, R^+, and R_X^+. The ionisation potentials of the corresponding radicals can serve as a measure of the stability of the carbonium ions[150]. The ions which may be regarded as products of the ionisation of the radical with the lowest ionisation potential are the most stable.

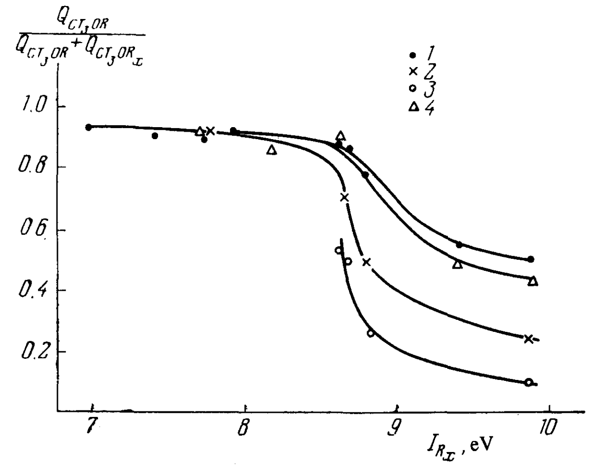


Figure 2. Dependence of the relative yields of the products of the interaction of methyl cations with the ethers ROR_X on the ionisation potentials of R_X: 1) CH_3OR_X; 2) $C_2H_5OR_X$; 3) $C_3H_7OR_X$; 4) $C_6H_5OR_X$.

Within the limits of each of the series of ethers ROR_X investigated, reactions (15b) and (15c) lead to the formation of the same charged fragments (CT_3^+ and R^+). Different R_X^+ ions are formed only in reaction (15a) for different initial ethers. It might have been expected that the stability of these ions will largely determine the mode of fragmentation of the intermediate oxonium ion. Indeed, it is seen from Table 15 that, when methyl cations interact with the ethers ROR_X, the relative yields of the ethers CT_3OR vary in parallel with the ionisation potentials of the groups R_X. Fig. 2 presents a graphical representation of the variation of these quantities for the reaction of methyl cations with ethers. Evidently the yields of the ethers $ROCT_3$ vary in accordance with a nearly exponential law up to a certain value of I_{R_X} (above 8.6 eV) and then remain virtually constant as the ionisation potentials are varied further. In order to account for the absence of a dependence of the yield of products on the ionisation potentials of the radicals when $I < 8.6$ eV, one can make the following assumption. The β-decomposition of tritium in CT_4 may lead to the formation of a certain amount of methyl cations. These cations react with the ethers and give rise to highly excited oxonium ions whose fragmentation proceeds via different pathways having equal probabilities.

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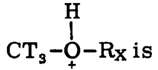
† The excitation energy of the transition complex is determined by the excitation energy of the carbonium ion and its affinity for the ether molecule. The latter exceeds 100 kcal mole^{-1} for the majority of the reactions investigated[148].

The absence of labelled ethers among the products of the interaction of methyl cations with alcohols shows that the monomolecular abstraction of the thermodynamically relatively unstable H^+ ion from the intermediate hydrodialkyloxonium ion  $CT_3-\overset{\overset{\displaystyle H}{|}}{\underset{+}{O}}-R_X$ is an unlikely process compared with the abstraction of the much more stable R_X^+ ion. In the reactions of methyl cations with aromatic ethers, account must be taken of the possibility of the alkylation of the aromatic ring. These processes will be discussed in greater detail below.

(b) The reactions of carbonium ions with halogen compounds. The results of a study[145] of the ion–molecule reactions of methyl cations with halogen halides (HCl, HBr, and HI) and ethyl halides (C_2H_5Cl, C_2H_5Br, and C_2H_5I) are presented in Table 16.

Table 16. The products of the interaction of methyl cations CT_3^+ with hydrogen halides and ethyl halides.

Initial cpd.	Yields, %			
	CH_3X	C_2H_5X	изо-C_3H_7X	н-C_3H_7X
HCl	100	—	—	—
HBr	100	—	—	—
HI	100	—	—	—
C_2H_5Cl	15±1	49±2	25±2	11±3
C_2H_5Br	37±1	43±2	20±3	—
C_2H_5I	100	—	—	—

It is seen from the data in Table 16 that the reactions of methyl cations with hydrogen halides lead to the formation of the corresponding labelled methyl halides, while the reactions of these species with ethyl halides give rise to methyl, ethyl, and propyl halides.

There is no doubt that the first stage in these reactions is the interaction of the free *p* orbital of the carbonium ion with the lone electron pairs of the halogen atoms. The interaction results in the formation of the corresponding halogenonium ions $[CT_3XR]^+$. The monomolecular decomposition of the complex $[CT_3XR]^+$ can proceed via two pathways. The first pathway involves the reaction which is the reverse of the process investigated. On the other hand, the transformation of the complex via the second pathway

$$[CT_3XR]^+ \begin{array}{l} \overset{1}{\nearrow} RX + CT_3^+ \\ \underset{2}{\rightarrow} CT_3X + R^+ \end{array}$$

leads to the formation of the corresponding labelled methyl halide. This mechanism of the formation of tritium-containing methyl halide may be adopted only for the reactions of methyl cations with ethyl halides. On the other hand, the heat of reaction of CT_3^+ with hydrogen halides,

$$CT_3^+ + HX \rightarrow CT_3X + H^+$$

is approximately 100 kcal $mole^{-1}$, which implies that the transformation of the 'onium ion proceeds monomolecularly. In order to account for the mechanism of the formation of labelled methyl halides, one could resort to processes involving bimolecular fragmentation of the intermediate ions:

$$CT_3\overset{+}{X}H + HX \rightarrow CT_3X + H\overset{+}{X}H \quad .$$

However, comparison of the proton affinities of hydrogen halides and the corresponding methyl halides showed that this reaction is also energetically unfavourable. Indeed, the proton affinities of HCl, HBr, and HI are 140, 141, and 145 kcal $mole^{-1}$,[151] while the affinities of CH_3Cl, CH_3Br, and CH_3I are 160, 163, and 170 kcal $mole^{-1}$ respectively[152]. The mechanism of the formation of methyl halides in the gas-phase interaction of methyl cations with hydrogen halides therefore still remains obscure.

(c) Reactions of carbonium ions with nitrogen compounds. Only one study has been published so far[146] in which gas-phase reactions of free carbonium ions with the given class of compounds were investigated. These are the reactions of methyl cations with diethylamine (Table 17).

Table 17. The products of the interaction of methyl cations CT_3^+ with diethylamine.

Product	Yield, %	Product	Yield, %
Diethylamine	26±1	Ethylpropylamine	10±1
Diethylmethylamine	55±1	Ethylisopropylamine	9±1

The main products of the reaction of methyl cations with diethylamine are labelled diethylamine, diethylmethylamine, ethylpropylamine, and isopropylamine. The formation of these products cannot be accounted for in terms of the mechanisms which we invoked in the discussion of the reactions of carbonium ions with other classes of compounds. This can probably be explained by the fact that, in contrast to the other substances investigated, the amines are characterised by the highest proton affinities (> 215 kcal $mole^{-1}$).[153] By virtue of this feature and also by virtue of the relatively low proton affinity of the methylene group (120 kcal $mole^{-1}$),[153] the most characteristic reaction in this case is apparently the exothermic proton transfer from the methyl cation to the amine molecule and not the formation of the intermediate ammonium ion:

$$CT_3^+ + (C_2H_5)_2NH \rightarrow CT_2 + [(C_2H_5)_2NTH]^+ \quad .$$

The subsequent reactions of the tritium-containing methylene group and the diethylammonium ion make it possible to explain the formation of all the products detected. Thus the isotope exchange reaction

$$(C_2H_5)_2NTH^+ + (C_2H_5)_2NH - (C_2H_5)_2NT + (C_2H_5)_2\overset{+}{N}H_2$$

leads to the formation of the labelled initial diethylamine, while the reactions involving the insertion of methylene groups in various bonds of the amine molecule‡ give rise to the other products detected.

4. Reactions of Carbonium Ions with Compounds whose Molecules Contain Several Nucleophilic Centres

In the study of ion–molecule reactions of this type, methyl cations were used as the molecular ions and the starting materials consisted of a number of organic compounds whose molecules contained an aromatic ring and

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‡ Similar reactions are well known in the chemistry of carbenes[154,155].

atoms with lone electron pairs. Such substances include bromobenzene[156], nitrobenzene[157], and alkyl phenyl and alkyl benzyl ethers[144].

The results obtained in the above studies show that the interaction of methyl cations with compounds of the given group leads to the formation of two types of products. One type comprises products resulting from the alkylation of the aromatic ring and the other comprises compounds whose formation involves attack by methyl cations on the lone electron pair. Thus, in the ion–molecule reactions considered here, there is competition between the interactions of methyl cations with the π electrons of the aromatic ring and with the free electron pairs of the substituent atoms.

Table 18 lists the intramolecular competition factors f_{comp}, which are defined as the ratios of the yields of the products of the interaction of methyl cations with the lone electron pairs (Q_p) to the yields of the products of the interaction with the π electrons of the aromatic ring (Q_π). It follows from Table 18 that, in the interactions of free methyl cations with the compounds investigated, the lone electron pairs of the substituent atoms are more reactive than the π electrons of the aromatic ring. The reactivities of the free electron pairs of bromine atoms, the nitro-group, and ether oxygen in alkyl benzyl ethers are similar, but much lower than the reactivities of the lone electron pairs of the oxygen atoms in alkyl phenyl ethers.

Table 18. The relative yields of the products of competing reactions and competition factors.

Starting material	Q_p, %	Q_π, %	f_{comp}
C_6H_5Br	65	35	1.86
$C_6H_5NO_2$	65	35	1.86
$CH_3OCH_2C_6H_5$	58	42	1.38
$C_2H_5OCH_2C_6H_5$	64	36	1.78
$CH_3OC_6H_5$	80	20	4.00
$C_4H_9OC_6H_5$	82	18	4.55
iso- $C_5H_{11}OC_6H_5$	88	12	7.34

Presumably the observed changes in the competition factor are associated with the changes in the ratio of the basicities of the nucleophilic centres in these compounds. However, one should note that studies on the relative basicities of the nucleophilic centres in a single molecule have not been made. We believe that extremely valuable information in this field of theoretical chemistry can be obtained with the aid of the radiochemical method considered here for the investigation of ion–molecule reactions.

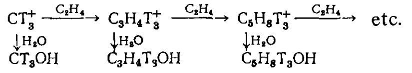
5. Competitive Reactions of Carbonium Ions

The possibility of using the radiochemical method for the study of competitive intermolecular reactions may be demonstrated by the results of a recent study of the gas-phase reactions of methyl cations with ethylene–water mixtures for different molar ratios of the components, namely $[C_2H_4]:[H_2O] = 1:1,\ 2:1,\ 3:1,\ 4:1$, and $5:1$.[158] It was established that the main products of these reactions are aliphatic alcohols.

The carbonium ions generated in unsaturated hydrocarbons are known[159] to initiate cationic polymerisation reactions. When methyl cations are generated in ethylene, these reactions can be represented by the equation

$$CT_3^+ + CH_2{=}CH_2 \rightarrow CT_3CH_2CH_2^+ \xrightarrow{C_2H_4} CT_3(CH_2)_3CH_2^+ \text{ etc.} \qquad (16)$$

For a reaction mixture containing water molecules, two competing processes will occur: the polymerisation reaction (16) and the reactions with water of all the varieties of the carbonium ions produced, leading to the formation of alcohols:



$$\begin{array}{llll} CT_3^+ \xrightarrow{C_2H_4} & C_3H_4T_3^+ \xrightarrow{C_2H_4} & C_5H_8T_3^+ \xrightarrow{C_2H_4} & \text{etc.} \\ \downarrow{\scriptstyle H_2O} & \downarrow{\scriptstyle H_2O} & \downarrow{\scriptstyle H_2O} & \\ CT_3OH & C_3H_4T_3OH & C_5H_8T_3OH & \end{array} \qquad (17)$$

With increase of the concentration of ethylene, an increase of the contribution of reaction (16) may be expected and hence an increase of the yield of alcohols with a larger number of carbon atoms. Experimental data confirm this hypothesis.

It is noteworthy that straight-chain alcohols were not detected among the products of the reactions of the intermediate carbonium ions, although the formation of such alcohols might have been expected bearing in mind the position of the carbonium centre at the instant of formation of these ions. This experimental finding permits the conclusion that there is sufficient time for the cations formed in reaction (16) to isomerise to thermodynamically more stable structures. Similar isomerisation reactions of carbonium ions are well known in organic chemistry.

It is also interesting that, for all the $[C_2H_4]:[H_2O]$ ratios, the yield of labelled methanol exceeds the value which might have been expected for a statistical mechanism of reactions (17). For example, for an equimolar ethylene : water ratio, a 50% yield of methanol could have been expected. The experimental yield (82.5%) greatly exceeds this value. The data obtained make it possible to estimate the competition factor for the reaction of methyl cations with methylene and water: $f_{\text{comp}} \simeq 4$. The higher reactivity of methyl cations in relation to water molecules compared with their reactivity in relation to ethylene molecules is due to the higher affinity of the CH_3^+ ions for H_2O (82 kcal mole^{-1})[148] compared with their affinity for C_2H_4 (69.5 kcal mole^{-1}).[160]

Analogous studies on the competitive reactions involving a wider range of substances will make it possible, in our view, not only to determine the competition factors in such reactions but also to supplement the nucleophilicity scale for substances, the construction of which is based on the equation $\lg(k_P/k_{H_2O}) = Sn$, where k_P/k_{H_2O} is the competition factor for the reactions of the carbonium ion with a base P and water, n is the nucleophilicity constant, and S the constant characterising the substrate[161].

VI. PROSPECTS FOR THE USE OF THE RADIOCHEMICAL METHOD OF INVESTIGATING ION–MOLECULE REACTIONS

On the basis of the theoretical considerations discussed previously and the experimental results published at the present time, one may reach certain conclusions about the scope of the radiochemical method for the investigation of ion–molecule reactions and about the prospects for its application in studies on the chemistry of molecular ions.

One of the most important features of this method is the possibility of obtaining molecular ions having the desired composition, structure, and initial location of the charge.

The composition and structure of molecular ions are determined by the composition and structure of the initial tritiated compounds and the initial location of the charge depends on the position of the tritium atom in these compounds.

The employment of the covalent tritides of certain elements as the initial compounds makes it possible to obtain the isosteric molecular ions of these elements (with a sextet of outer electrons), which are analogues of carbonium ions. As an example, we shall quote certain mechanisms for the formation of nitrogen-, oxygen-, and silicon-containing analogues of carbonium ions:

$$NT_3 \xrightarrow{-\beta^-} \bar{N}T_2^+ + He \quad ,$$
$$T_2O \xrightarrow{-\beta^-} TO^+ + He \quad ,$$
$$SiT_4 \xrightarrow{-\beta^-} SiT_3^+ + He \quad .$$

It should be noted that tritium-containing compounds, behaving as radiochemical sources of molecular ions, are characterised by a constant and prolonged action. They can be used for several years.

The radiochemical method leads to considerable possibilities not only for the generation of unique charged molecular species but also for the investigation of their chemical behaviour under a wide variety of conditions. This method makes it possible to investigate the reactions of molecular ions both with any individual substances and with their mixtures. A characteristic feature of the method is also the possibility of carrying out ion–molecule reactions in any state of aggregation.

The ion–molecule reactions initiated by the β-decomposition of tritiated compounds can be used to solve many important chemical problems. Such reactions can be applied in the experimental study of the relative basicities of substances (intermolecular competing reactions). Labelled electrophilic species constitute a kind of detector of electron densities in the molecule (intramolecular competing reactions).

Furthermore, ion–molecule reactions can be used to study processes where the involvement of molecular ions is postulated and also to study the individual stages of cationic polymerisation reactions.

The reactions of tritium-containing molecular ions have found application in the synthesis of a wide variety of tritiated compounds[162].

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Intermolecular Photochemical Reduction of Aromatic Nitro-compounds

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The current data on the intermolecular photochemical reduction of aromatic nitro-compounds under various conditions are considered and the mechanism of the primary stage of the photoprocess in neutral, acid, and basic media is discussed. The dependence of the photochemical reactivity of nitro-compounds on the characteristics of the structure of their excited state is examined.

The bibliography includes 113 references.

CONTENTS

I. INTRODUCTION

The present review considers data on the intermolecular photochemical reduction of aromatic nitro-compounds (aliphatic nitro-compounds and intramolecular photochemical reduction of aromatic nitro-compounds have already been reviewed[1,2]).

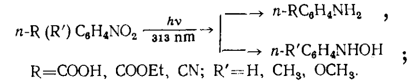
The results of the first systematic studies on the photochemical reduction of nitro-compounds were published in the middle 1960s,[3-6] although isolated studies had been published before that[7-9]. Photochemical reduction of nitro-compounds is briefly considered in Morrison's review[1]. Numerous studies concerned with the synthetic aspects and mechanism of photochemical reduction have now been made and are discussed in the present paper.

It follows from the published data that the composition and yield of the products of the photochemical reduction of many nitro-compounds depend on the reaction conditions. These differences are associated with changes in the photochemical reduction mechanism. In Morrison's review[1], the mechanism of the photochemical reduction of nitro-compounds is treated as one involving the homolytic abstraction of a hydrogen atom from a solvent molecule excited by a molecule of the nitro-compound. However, this mechanism probably operates only in neutral alcoholic and ethereal solutions. There is reason to believe that in acid and alkaline media the process proceeds via a two-stage heterolytic mechanism with initial electron transfer followed by proton transfer. In the present review, it is shown how ideas have developed about the mechanism of the photochemical reduction of nitro-compounds in neutral, acid, and alkaline media.

II. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS BY HYDROGEN DONORS (PHOTOCHEMICAL DEHYDROGENATION)

It has been established that aromatic nitro-compounds give rise to amino- and hydroxylamino-compounds on irradiation in protic solvents. When nitrobenzene is irradiated in 2-propanol by light at a wavelength of 366 nm, it is reduced to phenylhydroxylamine[3] with a quantum yield of 1.14×10^{-2}. As a result of the subsequent dark oxidation reactions and condensation with the reformed nitrobenzene, the final product is azoxybenzene. α-Nitrosonaphthalene is unreactive under these conditions[10], but is reduced on irradiation with light at a wavelength of 366 nm in benzene in the presence of a hydrogen donor stronger than 2-propanol, namely tri-n-butyltin[11]. The photochemical reaction product, α-naphthylamine, was identified from its fluorescence spectrum. In contrast to α-nitronaphthalene, the β-isomer is reduced in 2-propanol and β-naphthylhydroxylamine is formed with a quantum yield of 0.037.[12]

Nitrobenzoate esters are reduced to amines on irradiation in ethanol[13] and esterification and transesterification are observed; the yield of the amines is 13–40%. Other *p*- and *m*-derivatives of nitrobenzene undergo similar reactions[14,15]:



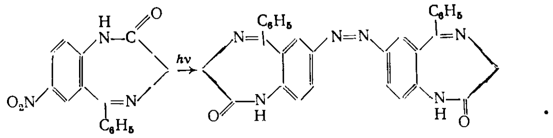
$$n\text{-R(R}')\text{C}_6\text{H}_4\text{NO}_2 \xrightarrow[313\ \text{nm}]{h\nu} \left[\begin{array}{l} \longrightarrow n\text{-RC}_6\text{H}_4\text{NH}_2\ , \\ \longrightarrow n\text{-R}'\text{C}_6\text{H}_4\text{NHOH}\ ; \end{array}\right.$$

R=COOH, COOEt, CN; R'=H, CH_3, OCH_3.

The photolysis was carried out in 2-propanol in an atmosphere of nitrogen at room temperature. The quantum yield of the reaction, determined spectrophotometrically from the decrease in the amount of the initial nitro-compound, is 0.12–0.45 for electron-accepting substituents (R) and 0.02–0.03 for electron-donating substituents (R'). *p*-Nitrophenol and *p*-nitroaniline are not reduced under these conditions[15]; however, photochemical reduction does occur when the amino-group is acylated[15,16]. It has been shown[14,15] that the quantum yield in the photochemical reduction of substituted nitrobenzenes in 2-propanol is satisfactorily correlated with the Hammett σ constants.

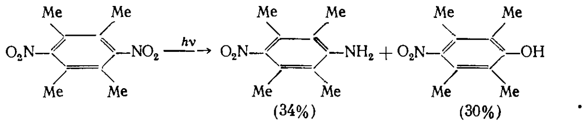
m-Dinitrobenzene and 1,3,5-trinitrobenzene are reduced photochemically in ethanol, the yield of the corresponding azoxy-derivatives not exceeding 2 %.[4] A similar process takes place in tetrahydrofuran. The final products were isolated by thin-layer chromatography. It has been established that ethanol is then oxidised to acetaldehyde[4].

On irradiation with light filtered through Pyrex glass in tetrahydrofuran, 7-nitro-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepin-2-one gives a 10% yield of an azo-compound[16]:

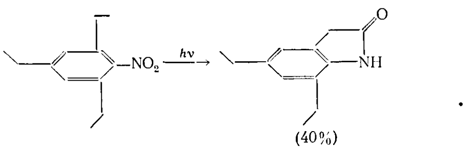


The reaction product was identified by its elemental composition and infrared, ultraviolet and mass spectra.

It is of interest that the photolysis in isopropyl alcohol of *p*-nitroacetophenone gives rise to a product resulting from the reduction of the nitro-group and not the keto-group, namely 4,4-diacetylazoxybenzene, in 31% yield[17]. The photochemical reduction of the sterically shielded nitro-group in 2-propanol has been investigated[18] and it has been shown that, together with the reduction process, the nitro-group is substituted by the hydroxy-group:



If the alkyl substituent in the *ortho*-position with respect to the nitro-group has a *β*-carbon atom, the photochemical reduction probably proceeds intramolecularly, for example[18]:



It has been reported[6] that 1,2,3,4-tetramethyl-5,6-dinitrobenzene is reduced photochemically in anhydrous ether to 1,2,3,4-tetramethyl-5-nitroaniline in 25% yield. The reaction was carried out with irradiation by the light of a 450 W mercury lamp at 2–6°C with stirring by a stream of nitrogen. The products were isolated by thin-layer chromatography and identified by ^{1}H NMR and from the elemental composition and mass spectra.

On irradiation with light filtered through Pyrex glass in ether, *p*-nitroanisole is reduced to *p*-anisidine (30%) and 4,4′-dimethoxyazoxybenzene (12%).[19] Under these conditions, nitrobenzene yields 44% of aniline, 2% of azobenzene, and 1% of 2-hydroxyazobenzene[19].

Heterocyclic compounds behave on photolysis similarly to nitro-compounds of the benzene series. It has been shown[5,20–22] that 4-nitropyridine *N*-oxide is converted quantitatively into the corresponding hydroxylamine on irradiation in absolute ethanol. Similar results were obtained for 4-nitro-derivatives of the *N*-oxides of *α*-picoline and 2,6-lutidine[5]. The experiments were performed in an atmosphere of nitrogen; after irradiation in the presence of oxygen, unidentified products having a different composition are formed.

Thus the photochemical reduction of nitro-compounds in a series of protic solvents proceeds comparatively readily. t-Butyl alcohol does not promote the occurrence of the reaction[13,19].

Qualitative aspects of the photochemical reduction by hydrogen donors have been considered in the studies described above. We shall now examine the available data concerning the nature of their reactive excited state and the mechanism of photochemical dehydrogenation.

1. The Multiplicity of the Excited State in the Photochemical Dehydrogenation Reaction

A characteristic feature of nitro-compounds is the comparative ease of the transition from the singlet to the triplet excited state and vice versa. The quantum yield in the formation of triplets is 0.6–0.8,[10,23] regardless of the configuration of the triplet state (n, π^* or π, π^*). Bearing in mind the longer lifetime of the triplet state compared with the singlet state, nitro-compounds in the triplet state are presumably involved in photochemical reduction.

This conclusion, based on the work of Brown and Williams[24], was reached in Morrison's review[1]. The evidence available at present for the involvement of the triplet state (T) in the photochemical reduction of nitro-compounds can be divided into two groups. They are based on (1) information about the chemical reactivity of nitro-compounds in the T state according to flash photolysis data[25] and (2) a comparison of data for the sensitisation or inhibition of the formation of the T state (from ESR [24] and phosphorescence spectra[26]) and the photochemical reduction reaction; in a number of studies the conclusions concerning the involvement of the T state in the reaction is based on experiments designed to investigate the influence of the donors and acceptors of the energy of triplet excitation on the quantum (chemical) yield of the reaction[3,12,19].

(1) The triplet–triplet absorption spectra of *α*- and *β*-nitronaphthalenes have been described[25,27,28]. Capellos and Porter[25] determined by the method of laser photolysis the rate constant for the abstraction of hydrogen from ethanol by *α*-nitronaphthalene (10^4 M^{-1} s^{-1}) and nitrobenzene (10^6 M^{-1} s^{-1}) in the T state. The photochemical dehydrogenation rate constant for nitrobenzene in the excited state[10], found from the dependence of the photochemical reduction quantum yield on the concentration of the alcohol (2-propanol), is 0.8×10^6 M^{-1} s^{-1}. The agreement between the constants determined by different methods is satisfactory and is consistent with the conclusion[10] concerning the triplet nature of the reactive state in photochemical reduction.

(2) Perfluoronaphthalene, the singlet level of which is higher and the triplet level (E_T = 56 kcal mole^{-1}) is lower than for nitrobenzene (E_T = 60 kcal mole^{-1}), has been used as an inhibitor of the photochemical reduction of nitrobenzene[24]. The irradiation was carried out with light at a wavelength >330 nm, which is not absorbed by perfluoronaphthalene, in degassed tetrahydrofuran solutions at room temperature. Following irradiation in the absence of inhibitors, the authors observed an ESR spectrum, which they attributed to the radical $C_6H_5N\dot{O}_2H$. In the presence of 0.1 M perfluoronaphthalene, the photochemical reduction of nitrobenzene did not occur. Under these conditions, the solution in tetrahydrofuran at –160°C gives rise to the ESR spectrum resulting from the formation of perfluoronaphthalene in the triplet state.

It has been shown[26] that 4-nitropyridine *N*-oxide (E_T = 52 kcal mole^{-1}) quenches the phosphorescence of diacetyl (E_T = 56.3 kcal mole^{-1}) in degassed solutions in ethanol and 2-propanol at room temperature. When a mixture of diacetyl and 4-nitropyridine *N*-oxide in alcohol is irradiated with light at a wavelength exceeding 400 nm, which is absorbed by diacetyl alone, the product is 4-hydroxyaminopyridine *N*-oxide. The results of the above studies[24,26] can be explained within the framework of the hypothesis of the triplet energy transfer leading to the T state of the nitro-compounds.

It has been concluded in a number of investigations that oxygen influences the photochemical reduction of nitro-compounds. Thus the quantum yield for the formation of phenylhydroxylamine by the reduction of nitro-benzene in 2-propanol is 1.14×10^{-2} in degassed solutions and 0.87×10^{-2} in air-saturated solutions[3]. The photochemical reduction of β-nitronaphthalene is also suppressed in the presence of oxygen[12].

According to Barltrop and Bunce's data[19], the yield of aniline in the photolysis of nitrobenzene (E_T = 60 kcal mole^{-1}) in ether in the presence of a fourfold excess of benzophenone (E_T = 69 kcal mole^{-1}), with almost complete absorption of the incident light by benzophenone, increases by a factor of six. Diacetyl and octafluoronaphthalene inhibit the photochemical reduction reaction[19]. Similar inhibition occurs also in the reduction of β-nitronaphthalene in the presence of cyclohexa-1,3-diene[12].

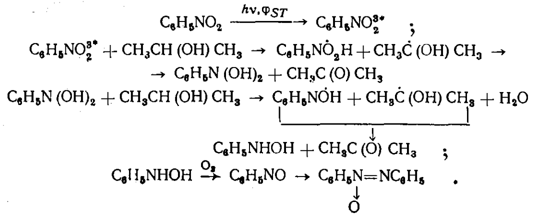
In the discussion of data based on the inhibition and sensitisation of a chemical process, one must bear in mind the multistep mechanism of the photochemical reduction (see below) and hence the possible influence of organic excitation energy acceptors or oxygen not only on the triplet state deactivation stage but also on the secondary thermal processes involving radical species. The above investigations did not yield unambiguous evidence showing that the sensitisation of the photochemical reduction reaction is in fact due to the triplet–triplet energy transfer. The conclusions concerning the triplet nature of the reactive state of nitro-compounds in photochemical dehydrogenation reactions, based on the above results[3,12,19], are therefore tentative.

2. The Photochemical Dehydrogenation Mechanism

Yet another feature is characteristic of nitro-compounds in the n, π^* excited triplet state. The structure of the nitro-group in this state is such that its chemical properties resemble those of a "biradical"[1], like the carbonyl group in the triplet state of ketones[29]. It has been shown for ketones[30,31], that the properties of the reacting triplet state and of the t-butoxy-radical vary in parallel in hydrogen abstraction reactions.

The mechanism of photochemical reduction in protic solvents, including as a primary step the abstraction of a hydrogen atom from the alcohol by the nitrogen-compound in the excited triplet state n, π^*, has been considered[1,3] in conformity with the foregoing considerations:

Scheme 1



$$C_6H_5NO_2 \xrightarrow{h\nu, \varphi_{ST}} C_6H_5NO_2^{3*} \quad ;$$
$$C_6H_5NO_2^{3*} + CH_3CH(OH)CH_3 \rightarrow C_6H_5N\dot{O}_2H + CH_3\dot{C}(OH)CH_3 \rightarrow$$
$$\rightarrow C_6H_5N(OH)_2 + CH_3C(O)CH_3$$
$$C_6H_5N(OH)_2 + CH_3CH(OH)CH_3 \rightarrow \underbrace{C_6H_5N\dot{O}H + CH_3\dot{C}(OH)CH_3}_{\downarrow} + H_2O$$
$$C_6H_5NHOH + CH_3C(O)CH_3 \quad ;$$
$$C_6H_5NHOH \xrightarrow{O_2} C_6H_5NO \rightarrow \underset{\underset{O}{\downarrow}}{C_6H_5N{=}NC_6H_5} \quad .$$

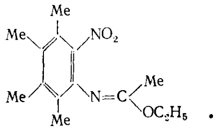
According to Scheme 1, phenylhydroxylamine is formed without a stage involving the formation of nitrosobenzene, which is believed[3] to be produced by the oxidation of phenylhydroxylamine by the dissolved oxygen.

It has been shown[19] that the photolysis of phenylhydroxylamine in ether leads to the formation of aniline in 42% yield. When an ethereal solution of nitrobenzene is irradiated with light filtered through Pyrex glass, aniline is again formed, but under these conditions nitrosobenzene is converted into azoxybenzene[19]. A similar result was obtained in the photolysis of nitrosobenzene in methanol[32]. These results lead to the conclusion, in agreement with Scheme 1, that nitrosobenzene does not constitute an intermediate stage in the photochemical reduction of nitrobenzene to phenylhydroxylamine.

However, it has been established recently that, when deoxygenated dilute (10^{-3}–10^{-5} M) solutions of nitrosobenzene in 2-propanol are irradiated, phenylhydroxylamine is formed with a quantum yield of 0.047.[33] The photolysis of concentrated nitrobenzene solution gave azoxybenzene. The latter process has probably been observed in earlier investigations[19,32]. In the light of these data, Scheme 1 may not reflect quite accurately the sequence of reactions involving the formation of the intermediates in the photochemical reduction.

We shall now consider data confirming qualitatively certain details of Scheme 1. The abstraction of a hydrogen atom from the solvent by an excited molecule of the nitroso-compound is indicated by the dependence of the quantum yield of the photochemical reduction of p-nitrobenzonitrile on the C–H bond energy of the reducing agent: the quantum yield of this reaction decreases on passing from 2-propanol to ethanol and hexane[15]. Similar data have been published for m-dinitrobenzene[34]. It has been established[34] that the efficiency of the photochemical reduction of p-dinitrobenzene decreases on passing from CH_3OH to CD_3OD, the isotope effect being $K_H/K_D \simeq 2.6$.

The photolysis of 1,2,3,4-tetramethyl-5,6-dinitrobenzene in ether yielded[6] compound (I), which is a product of the recombination of the radicals formed in the photochemical dehydrogenation of ether by the nitro-compound:



(I)

The structure of compound (I) was confirmed by infrared spectroscopy, ^1H NMR, and elemental analysis. Its formation is consistent with the radical mechanism for the primary step of the photochemical reduction in protic media.

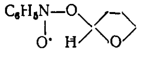
The formation of phenyl nitroxide $C_6H_5N\!\left\langle\begin{matrix}H\\ O^{\cdot}\end{matrix}\right.$ (Scheme 1) in the photolysis of nitrobenzene in secondary alcohols and tetrahydrofuran follows from a number of data[35-37]. When photolysed in the cavity of a microwave spectrometer, the ESR spectrum is identical to that of phenyl nitroxide obtained in the photolysis of nitrosobenzene[35]. When nitrobenzene is irradiated in primary alcohols, the product is the radical $C_6H_5N(\dot{O})R$, while in secondary alcohols (in 2-propanol) $C_6H_5N\dot{O}H$ is formed. The radical $C_6H_5N(\dot{O})C(OH)(CH_3)_2$ was detected in a later investigation[37] involving the irradiation of nitrobenzene in 2-propanol.

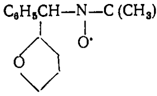
The detection of the primary photochemical reduction product, the $ArN\dot{O}_2H$ radical, would constitute direct confirmation of Scheme 1. Such confirmation has been obtained for the photochemical reduction of ketones. When benzophenone was irradiated with ultraviolet light in ethanol in the ESR spectrometer cavity, the simultaneous appearance of diphenyl hydroxymethyl and hydroxyethyl radicals was observed[38]:

$$(C_6H_5)_2CO^{3*} + CH_3CH_2OH \rightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}HOH \quad .$$

However, the analogous radical $C_6H_5N(\dot{O})OH$ derived from nitrobenzene has not yet been detected experimentally.

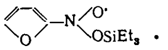
Ward[39] attributed the ESR signal obtained in the photolysis of nitrobenzene in tetrahydrofuran to the $C_6H_5N(\dot{O})OH$ radical. However, later studies[37,40] established that this signal is due to the $C_6H_5N\dot{O}_2R$ radical (II), which is formed when the tetrahydrofuryl radical reacts with nitrobenzene:


(II)


(III)

When the tetrahydrofuryl radical is removed from the system with the aid of a spin trap (t-butyl phenyl nitrone), the characteristic spectrum of radical (III) appears instead of the ESR spectrum obtained by Ward.

A radical of the $ArNO_2R$ type has been detected[41] following the irradiation of 2-nitrofuran in triethylsilane:



The attempts to obtain the $C_6H_5N\dot{O}_2H$ radical by the photolysis of nitrobenzene in the presence of other effective hydrogen donors were unsuccessful[35,40]. However, the $ArN\dot{O}_2H$ radical has been detected in the reaction of atomic hydrogen with solid nitrobenzene[42] and also in the low-temperature radiolysis of nitrobenzene[43]. Evidently it is rapidly destroyed under the photolytic conditions.

It has been suggested[37] that a radical of type $ArN\dot{O}_2R$ undergoes monomolecular decomposition:

$$ArN(\dot{O})OR \rightarrow ArNO + R\dot{O}$$

leading, as with the $ArN\dot{O}_2H$ radical, to the formation of the final reaction products.

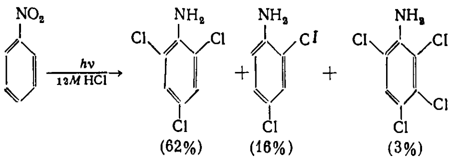
Thus the mechanism of the photochemical reduction, involving the abstraction of hydrogen from solvent molecules by the nitro-compound in the n, π^* triplet state, may be regarded as generally accepted.

The abstraction of hydrogen from alcohol molecules by nitro-compounds in the π, π^* triplet state was not observed until recently[1]. According to the latest data, 2-nitronaphthalene[12] and 4-nitropyridine Λ-oxide[26], which have the lowest π, π^* triplet level, are reduced on irradiation in 2-propanol. The quantum yield in the photochemical reduction of 2-nitronaphthalene is 0.037. Nitrobenzene in the n, π^* triplet state is reduced under these conditions with a quantum yield of 0.0114.[3] It is believed[12] that the rate of abstraction of hydrogen by 2-nitronaphthalene in the triplet state is lower by 3–4 orders of magnitude than for nitrobenzene, but the longer lifetime of the 2-nitronaphthalene triplets compensates the lower rate and leads to a comparatively high quantum yield in the photochemical reduction. Furthermore, one must bear in mind that the quantum yield is for the formation of the triplet states of 2-nitronaphthalene (0.83) is higher than for nitrobenzene (0.67).[10,23]

The low quantum yield in the conversion of nitrobenzene in 2-propanol into arylhydroxylamine [bearing in mind that the quantum yield in the transition of nitrobenzene to the excited state is 0.67 (Hurley and Testa[10]) and that the degree of conversion of $C_6H_5N(\dot{O})(OH)$ into C_6H_5NHOH is 100%] is evidently due to the fact that the deactivation of triplets predominates over the abstraction of hydrogen from the solvent. Thus it has been reported[11] that the lowest triplet state of nitrobenzene is of the n, π^* type and that the rate of abstraction of hydrogen atoms is high $(0.8 \times 10^6\ \mathrm{mole^{-1}\ s^{-1}})$.[10] The low quantum yield in the photochemical reduction of nitrobenzene is therefore associated, according to the authors[10], with the high rate of deactivation of the triplet state $(\sim 10^9\ \mathrm{s^{-1}})$.

III. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS IN AN ACID MEDIUM

Studies of the photochemical reduction of nitro-compounds in alcohols showed that the process proceeds more effectively when hydrochloric acid is added[44,45]. Thus the quantum yield in 50% aqueous isopropyl alcohol in an atmosphere of nitrogen increases from 1.14×10^{-2} in the absence of acid to 0.3 in the presence of 12 M HCl.[44] The initial product of the reduction of nitrobenzene in isopropyl alcohol in the presence of HCl is phenylhydroxylamine, which was determined polarographically[45]: the final products are aniline (40%), *p*-chloroaniline, and *p*-aminophenol. When nitrobenzene is irradiated in the presence of 12 M HCl but in the absence of alcohol, the reduction of the nitro-group is accompanied by the substitution of the hydrogen atoms in the benzene ring by chlorine[46]:



Similar results were obtained for *o*-, *m*-, and *p*-substituted nitrobenzenes[47]. The quantum yield in the photochemical reduction of nitrobenzene derivatives in water in the presence of 12 M HCl (determined from the decrease in the amount of the nitro-compound) depends only slightly on the electron-accepting properties of the substituent and decreases following the introduction of an electron-donating group into the ring[47].

On irradiation with light at a wavelength of 335 nm[48] in a hydrochloric acid–2-propanol mixture, α-nitronaphthalene is converted into α-naphthylamine in 70% yield. It has been shown[49] that the primary product of the photochemical reduction of α-nitronaphthalene under these conditions is α-naphthylhydroxylamine, which is converted in the presence of HCl into 4-chloro-1-naphthylamine. The latter is dechlorinated photochemically and yields α-naphthylamine. The quantum yield in the formation of 4-chloro-1-naphthylamine, identified from ultraviolet, infrared, and fluorescence spectra, increases in proportion to the concentration of HCl.[50] The maximum quantum yield was 1.28×10^{-2} for 6 M HCl in 50% aqueous 2-propanol solution, while in the alcohol in the absence of acid an appreciable photochemical reaction is not observed.

On irradiation in alcohol in the presence of HCl, 4-nitropyridine is converted into 4-hydroxyaminopyridine and 4,4′-azopyridine[51]. The quantum yield for the decrease in the amount of 4-nitropyridine rises to 0.94 with increase of HCl concentration[29,51]. According to the results of Cu and Testa[52], the limiting quantum yield in the photochemical reduction of 4-nitropyridine in 2-propanol in the presence of HCl is somewhat smaller, amounting to 0.65. The discrepancy between the quantum yields has been explained[52] by the difference between the two analytical methods used to determine the degree of conversion of the starting material (spectrophotometry[29] and polarography[52]).

Irradiation of 5-nitroquinoline in aqueous 2-propanol in the presence of HCl leads to the formation of 5-amino-6,8-dichloroquinoline[53]; the maximum quantum yield in the photochemical reduction is 5.44×10^{-2} at an HCl concentration $\geqslant 1$ M.

The linear dependence of the quantum yield in the photochemical reduction of α-nitronaphthalene on the HCl concentration led[50,51] to a mechanism for the photochemical reduction of nitro-compounds by isopropyl alcohol in an acid medium (Scheme 2), including a stage in which the excited triplet state is protonated (aromatic nitro-compounds in the ground state are weak bases):

Scheme 2

$$\mathrm{ArNO_2} \xrightarrow{h\nu,\varphi_{ST}} \mathrm{ArNO_2^{3*}} \quad ;$$

$$\mathrm{ArNO_2^{3*}} + \mathrm{H^+} \rightleftarrows \mathrm{Ar\overset{+}{N}O_2H^{3*}} \quad ;$$

$$\mathrm{ArNO_2^{3*}} \rightarrow \mathrm{ArNO_2} \quad ;$$

$$\mathrm{Ar\overset{+}{N}O_2H^{3*}} + \mathrm{(CH_3)_2CHOH} \rightarrow \underset{\substack{\downarrow \\ \text{reaction products.}}}{\mathrm{Ar\dot{N}O_2H}} + \mathrm{(CH_3)_2\dot{C}OH} + \mathrm{H}^{\cdot\cdot}$$

The quantum yield in the photochemical reduction of nitrobenzene is independent of HCl concentration up to 3 M, after which it increases linearly. Evidently the protonation of nitrobenzene in the *T* state begins to an appreciable extent only at HCl concentrations exceeding 3 M.[44]

Using the method of pulsed laser photolysis, Capellos and Porter[25] determined the rate constants for the protonation of α-nitronaphthalene (1.85×10^7 M^{-1} s^{-1}) and nitrobenzene (4.4×10^7 M^{-1} s^{-1}) in the *T* state, the values obtained being much greater than the dehydrogenation rate constants (10^4 and 10^6 M^{-1} s^{-1} for α-nitronaphthalene and nitrobenzene respectively[25]). These results agree indirectly with Scheme 2).

The completion of the photochemical reduction of the protonated triplet state should include an electron transfer stage. This process is probably unlikely, since alcohols, the ionisation potentials of which are 11–12 eV, are weak electron donors[54]. Data which cannot be accounted for by the mechanism of acid catalysis (Scheme 2) have been published recently. It has been shown[53,55,56] that catalysis is observed in the presence of HCl but not H_2SO_4. Since the hydrogen sulphate anion undergoes one-electron oxidation with greater difficulty than the chloride anion, the authors[55] suggested that the protonation in the presence of HCl is preceded by electron transfer from the chloride anion to the excited triplet state of the nitro-compound (Scheme 3):

Scheme 3

$$\mathrm{ArNO_2} \xrightarrow{h\nu,\varphi_{ST}} \mathrm{ArNO_2^{3*}} \quad ;$$

$$\mathrm{ArNO_2^{3*}} + \mathrm{Cl^-} \rightarrow [\mathrm{ArNO_2^{\dot{-}}} \ldots \mathrm{Cl^{\cdot}}] \quad ;$$

$$[\mathrm{ArNO_2^{\dot{-}}} \ldots \mathrm{Cl^{\cdot}}] + \mathrm{H^+} \rightarrow [\mathrm{Ar\dot{N}O_2H} \ldots \mathrm{Cl^{\cdot}}] \quad ;$$

$$[\mathrm{Ar\dot{N}O_2H} \ldots \mathrm{Cl^{\cdot}}] + \mathrm{CH_3CH(OH)CH_3} \rightarrow \underset{\substack{\downarrow \\ \text{reaction products.}}}{\mathrm{Ar\dot{N}O_2H}} + \mathrm{HCl} + \mathrm{CH_3\dot{C}(OH)CH_3}$$

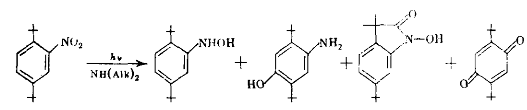
The conversion of the $\mathrm{Ar\dot{N}O_2H}$ radical into the final products can be described within the framework of Scheme 1.

An absorption spectrum with a maximum in the region of 440 nm has been obtained in the flash photolysis of degassed nitrobenzene solutions in aqueous 2-propanol in the presence of 6 M HCl. The authors attribute it[56] to the $\mathrm{C_6H_5\dot{N}O_2H}$ radical formed on protonation of the radical-anion. A similar result was obtained for 4-nitropyridine[56]. The authors[56] are inclined to favour a photochemical reduction mechanism resembling Scheme 3, although they were unable to measure the spectrum of the pair [$\mathrm{ArNO_2^{\dot{-}}}$ .. Cl] or the radical-anion $\mathrm{ArNO_2^{\dot{-}}}$ in acid media. The reason for this is probably the high rate of protonation of the radical-anion (for example, the rate constant for the protonation of the α-nitronaphthalene radical-anion is approximately 10^{10} M^{-1} s^{-1}).[25] On the other hand, there are literature data[57] demonstrating one-electron transfer from the chloride anion of the nitro-compound in the ground state (m-dinitrobenzene and trinitrobenzene), resulting in the formation of radical-anions. Similar data for the reaction in the excited state are lacking.

IV. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS IN AN ALKALINE MEDIUM

A series of studies on the photochemical reduction in alakaline media has shown that the composition of the reaction products and the kinetics are different from those in the photochemical reduction in neutral media. In alkaline media, the reduction process proceeds more effectively and the yield of products is higher than for the photochemical reduction in alcohols and ethers; instead of hydroxylamines and amines, final condensation products are obtained—azo- and azoxy-compounds. The yield of the azo-compound in the photolysis of 7-nitro-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepin-2-one in diethylamine is higher than in tetrahydrofuran (40% and 10% respectively)[16].

There are data showing that, on irradiation in neutral solutions, 1-t-butyl-2-nitrobenzenes give rise to intramolecular products only, namely indolinones (VII),[58-61] while in solutions in aliphatic amines products of the intermolecular reduction of the nitro-group are formed, i.e. hydroxylamines (V) and amines (VI):[59-62]



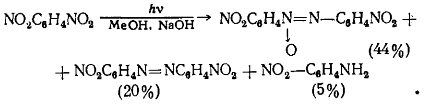
(IV) (V) (VI) (VII) (VIII) .

In the latter case, indolines (VII) and quinones (VIII) are formed as side products. The hydroxylamines (V) are converted into azoxy- and azo-compounds[59-61] and can also condense with amine oxidation products[62].

The photochemical reduction of a series of mononitro-compounds in alkylamines has been investigated[19] and it has been shown that the composition of the reaction products is more varied than in photochemical reduction in neutral media: the yield of arylamines varies from 6 to 22%, that of azo-compounds from 2 to 20%, that of azoxy-compounds from 5 to 35%, and that of o-hydroxyazo-compounds from 10 to 30%.

Aromatic amines may be used as reducing agents[63]. When m-chloronitrobenzene is irradiated in a benzene solution of N-methylaniline in an atmosphere of nitrogen, 37% of m-chloroaniline is formed; in the presence of NN-dimethylaniline, the yield of m-chloroaniline is 25%. Under these conditions, α-nitronaphthalene is converted into α-naphthylamine (37%) [63] and arylamines are oxidised, N-methylformanilide (34%) and N-methylaniline (56%) being fromed from NN-dimethylaniline.

An increase of the yield of the reduction products compared with alcoholic media is also observed in an alkaline alcoholic medium. The photolysis of m-dinitrobenzene in ethanol yields not more than 2% of an azoxy-compound[4], while irradiation in 50% aqueous methanol in the presence of 0.05 M NaOH gives a yield of reduction products up to 69%:[64,65]



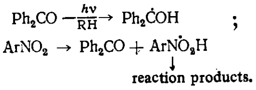
$$NO_2C_6H_4NO_2 \xrightarrow[\text{MeOH, NaOH}]{h\nu} \underset{\underset{O}{\downarrow}}{NO_2C_6H_4N}{=}N{-}C_6H_4NO_2 + \;(44\%)$$
$$+ \underset{(20\%)}{NO_2C_6H_4N{=}NC_6H_4NO_2} + \underset{(5\%)}{NO_2{-}C_6H_4NH_2} \quad .$$

A number of other mono- and di-nitro-compounds of the benzene and naphthalene series are also reduced under these conditions[65]. The photolysis of 5-nitro- and 8-nitro-anthraquinone-1-sulphonic acids in alkaline aqueous alcoholic solutions gives an approximately 3% yield of amino-anthraquinonesulphonic acids[66].

The sequence in which the photochemical reduction products are formed in an alkaline medium has been described[19]. It has been shown that irradiation with light at a wavelength ≤290 nm leads to the formation of anilines, while irradiation with light at a wavelength ≥290 nm results in the formation of azoxy- and azo-products. The experiments were carried out in the presence of oxygen, since it has an insignificant influence on the yield of the final product[19]. The irradiation of azo- and azoxy-benzenes under the experimental conditions leads to the formation of hydrazobenzene[67] and 2-hydroxyazobenzene[68] respectively. Aniline is also formed in small amounts under these conditions[19], but the process is much slower than the formation of anilines from hydroxylamines. The authors[19] therefore believe that anilines are formed on photochemical reduction mainly from the corresponding arylhydroxylamines and not from azo- and azoxy-derivatives. It has also been suggested that a nitroso-compound is formed as an intermediate before the hydroxylamine formation stage. Arylhydroxylamines and nitroso-compounds are unstable in alkaline media and condense with formation of azo- and azoxy-compounds, which has been established by special dark experiments[19,65].

Indirect data consistent with the involvement of nitro-compounds in the triplet state in photochemical reduction in alkaline media have been published[65,69]. A study has been made of the sensitisation of the photochemical reduction of 4,4′-dinitrobiphenyl (E_T = 58 kcal mole^{-1}) by naphthalene (E_T = 61 kcal mole^{-1}) and benzophenone (E_T = 69 kcal mole^{-1}).[65] The relative singlet levels in these pairs is not known accurately but, judging from the long-wavelength limit of the absorption spectra, the energy of the singlet state, at least in naphthalene, is higher than in 4,4′-dinitrobiphenyl. Irradiation was carried out with light at a wavelength of 254 nm, the ratio of the donor and acceptor concentrations being such that the main bulk of the exciting light (≥90%) is absorbed by benzophenone or naphthalene. Under these conditions, the quantum yield of the reaction, found from the decrease in the amount of the nitro-compound, is 0.056 in the absence of the sensitiser and 0.03 and 0.16 in the presence of naphthalene and benzophenone respectively.

The quantum yield and the photochemical reduction of 4-*NN*-diethylamino-4′-nitroazobenzene in butylamine increases from 4.2×10^{-4} to 0.14 when 0.27 M benzophenone is introduced[69]. These data can probably be accounted for by energy transfer via triplet levels. However, results have been published showing[69] that the sensitisation of the photochemical reduction of nitro-compounds by benzophenone may be to some extent also "chemical" sensitisation (for the description of its mechanism, see Monroe and Wamser[70]):



$$Ph_2CO \xrightarrow[RH]{h\nu} Ph_2\dot{C}OH \quad ;$$
$$Ph_2\dot{C}OH + ArNO_2 \rightarrow Ph_2CO + \underset{\underset{\text{reaction products.}}{\downarrow}}{ArN\dot{O}_2H}$$

It has been suggested[19,63] that photochemical reduction in both amines and alcohols proceeds via a mechanism involving the dehydrogenation of the amine by the nitro-compound in the triplet state, which leads to the formation of the $ArN\dot{O}_2H$ radical. However, this hypothesis is inconsistent with the results of other studies[10,19,63], where it has been shown that α-nitronaphthalene is not reduced in alcohol[10] but is reduced in amines[19,63].

α-Nitronaphthalene is known to have a π, π* lowest triplet state, which is relatively unreactive in hydrogen abstraction reactions[23,71]. Possibly the reduction of the π, π* triplets of nitro-compounds in alkaline media is facilitated by the occurrence of the process via a mechanism different from that of photochemical dehydrogenation. In this respect, the photochemical reduction of nitro-compounds in alkaline media resembles the photochemical reduction of ketones. Electron transfer with subsequent proton transfer in secondary processes has been suggested as the first stage in the reduction by alkylamines of excited states of ketones, which are unreactive in hydrogen abstraction reactions[72]. This is indicated by the chemical polarisation of electrons[73], observed on irradiation of the benzophenone–triethylamine system, and also by the decrease in the rate of photochemical reduction with increase in the ionisation potential of the amine[72].

Pacifici et al.[69] were the first to suggest that the reduction of nitro-compounds in amines proceeds via electron transfer from the solvent to the nitro-compound in the triplet state. The authors observed that the direction of the photochemical reaction of 4-*NN*-diethylamino-4′-nitroazobenzene in amines is different from that in alcohols. A hydrazo-compound (resulting from the reduction of the azo-group) is formed in alcohols, while in butylamine the reduction involves the nitro-group, the product—4-*NN*-diethylamino-4′-hydroxyaminoazobenzene—having been identified from the ultraviolet spectrum and its conversion into an azoxy-compound. The following reaction mechanism was proposed:

$$ArNO_2 \xrightarrow[\varphi_{ST}]{h\nu} ArNO_2^{3*} \quad ;$$

$$ArNO_2^{3*} + RNH_2 \rightarrow ArNO_2^{\dot{-}} + RNH_2^{\dot{+}} \quad .$$

The radical-anion of the nitro-compound abstracts a proton from the radical-cation of the amine:

$$ArNO_2^{\dot{-}} + RNH_2^{\dot{+}} \rightarrow ArN\dot{O}_2H + R\dot{N}H \quad .$$

The $ArN\dot{O}_2H$ radical is subsequently converted into the final products.

A similar mechanism has been proposed in another investigation[62], the difference being that the radical-anion of the nitro-compound and the radical-cation of the amine are believed by the authors to exist in the form of an ion pair, where proton transfer takes place.

There are data showing that photochemical reduction in alkaline alcoholic media also proceeds with electron transfer in the primary step[65]. It has been established that the quantum yield of the photochemical reduction of nitro-compounds in absolute alcohol in the presence of sodium alkoxide and in alkaline aqueous alcoholic media increases with increased concentration of the alkoxide ion[34,65]. According to ESR data, there is a simultaneous increase in the steady-state concentration of the radical-anions of the nitro-compounds[74]. These results have been explained by the participation of the alkoxide ion in the photochemical reduction, which involves one-electron transfer from the anion to the nitro-compound in the excited triplet state (Scheme 4):

Scheme 4

$$\mathrm{ArNO_2} \xrightarrow[\varphi_{ST}]{h\nu} \mathrm{ArNO_2^{3*}} \quad ;$$

$$\mathrm{ArNO_2^{3*}} + \mathrm{CH_3\overline{O}} \rightarrow [\mathrm{ArNO_2^{\dot{-}}} \ldots \mathrm{CH_3\dot{O}}] \quad ;$$

$$[\mathrm{ArNO_2^{\dot{-}}} \ldots \mathrm{CH_3\dot{O}}] \rightarrow \underset{\substack{\downarrow \\ \text{reaction products.}}}{\mathrm{ArN\overline{O}_2H}} + \mathrm{CH_2O}\ (\text{or}\quad \mathrm{ArN\dot{O}_2H} + e + \mathrm{CH_2O})$$

The radicals formed as a result of electron transfer are probably enclosed in a solvent cage, where hydrogen transfer takes place[65,74]. Hydrogen transfer may be promoted by the formation of the $\mathrm{CH_3\dot{O}}$ radical in a non-equilibrium state, which has excess vibrational energy. This scheme is consistent with the absence of an isotope effect in the photochemical reduction by $\mathrm{CH_3O^-}$ and $\mathrm{CD_3O^-}$ ions[34,74]. In contrast to photochemical dehydrogenation, where the ratio $K_H/K_D = 2.6$ for *p*-dinitrobenzene, in photochemical reduction in an alkaline medium $K_H/K_D = 1$ for *m*-dinitrobenzene and 1.4 for *p*-dinitrobenzene[34,74]. In the reduction by the alkoxide ion, the C–H bond energy in the reducing agent probably plays a secondary role. This conclusion can be explained on the hypothesis that the rate of reaction of the excited state of the nitro-compound with the alkoxide ion is diffusion-controlled and reduces to electron transfer in the primary step; the transfer of a hydrogen atom (proton) takes place in subsequent stages of the reaction, which are not kinetically controlled[34].

Data demonstrating the formation of radical-anions when the charge of a strong base is accepted by the nitro-compound provide a qualitative confirmation of Scheme 4 for the photochemical reduction of nitro-compounds in alkaline media[75–77]. On irradiation, the probability of electron transfer increases markedly[78,79]. According to data obtained by ESR, alkylamines[69] and alkali metal alkoxides[74,79] can play the role of reducing agents in electron phototransfer[74,79].

It has been noted[65] that nitro-compounds are reduced by the formate anion as well as alkoxide ions. The limiting quantum yield in the photochemical reduction of *m*-dinitrobenzene by sodium formate in water is 0.01.[34] *m*-Dinitrobenzene is not reduced by sodium acetate in water[65]. The authors explain this by the fact that, in contrast to acetate anions, alkoxide and formate anions behave as hydride ion donors. The transfer of a hydride ion can in principle proceed in stages, and may include electron transfer followed by the transfer of a hydrogen atom.

V. INTERMOLECULAR PHOTOCHEMICAL DEOXYGENATION AS A VARIETY OF PHOTOCHEMICAL REDUCTION

Intermolecular photochemical deoxygenation can be regarded as a kind of photochemical reduction process in which the reduction products are formed via the abstraction by the reducing agent of an oxygen atom from the nitro-group in the excited nitro-compound. The photochemical deoxygenation of nitro-derivatives by triethyl phosphite has been described[80].

It has been observed recently that nitrobenzene and some of its derivatives react with the cyanide ion under the influence of ultraviolet light and are converted into nitroso-compounds[81–83]:

$$\mathrm{ArNO_2} + \mathrm{CN^-} \xrightarrow{h\nu} \mathrm{ArNO} + \mathrm{OCN^-} \quad .$$

The reaction proceeds stoichiometrically and the quantum yield increases as the cyanide concentration rises to 1 M. Evidently nitrosobenzene is formed in the reaction of excited nitrobenzene with $\mathrm{CN^-}$.[83]

The photochemical deoxygenation occurring when the nitrobenzene–$\mathrm{BCl_3}$ complex is irradiated in cyclohexane has been described[84]; the quantum yield is 3.9×10^{-3}. The authors believe that electronic excitation leads to a weakening of the N–O bond of nitrobenzene and a strengthening of the O–B bond in the complex. The transfer of an oxygen atom from nitrobenzene to $\mathrm{BCl_3}$ is accompanied by the liberation of a chlorine atom, which gives rise to a chain process resulting in the formation of chlorocyclohexane and $\mathrm{H_3BO_3}$.

VI. SIDE REACTIONS ACCOMPANYING PHOTOCHEMICAL REDUCTION

The photochemical reduction of nitro-compounds is frequently complicated by side reactions, which may compete with the reduction process and sometimes become fully dominant. The photochemical reactions involving substituents in the nitro-compound (photochemical dehalogenation, photochemical rearrangement of benzoate esters, hydrolysis of the nitrile group, etc.) are not considered here. Under the conditions of "reducing photolysis", the nitro-group itself can undergo photochemical denitration, or photochemical substitution, or can be converted into a nitrite. These processes sometimes completely suppress the photochemical reduction of the nitro-group.

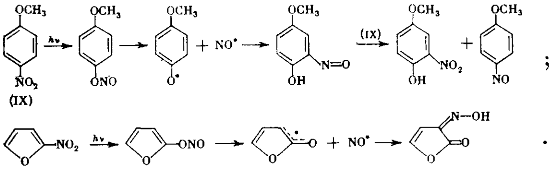
Photochemical denitration of nitro-compounds has been observed in the photolysis of isomeric chloro- and bromo-nitrobenzenes in an aqueous alcoholic solution of sodium nitrite[85]. Taking into account the results of El'tsov et al.[86], the nitro-group is presumably reduced under photolysis conditions to an amino-group, the latter is diazotised, and the diazo-group formed is substituted by hydrogen. Photochemical denitration by sodium tetrahydroborate has been observed in the photochemical reduction of certain nitro-compounds: *α*-nitronaphthalene 4-methoxy-1-nitronaphthalene, and 1-nitropyrene[82].

Certain aromatic nitro-compounds can not only reduce the nitro-group but can also participate in the photochemical substitution of the nitro-group by cyano-, methoxy-, hydroxy-groups, etc. Thus *α*-nitronaphthalene and *p*-nitroanisole are reduced to the amines on irradiation in aliphatic amines[19], while in the presence of $\mathrm{CN^-}$, $\mathrm{CH_3O^-}$, and $\mathrm{OH^-}$ ions they are involved in nucleophilic photochemical substitution reactions[81,87,88]. In the presence of HCl, 1-nitronaphthalene, 1,5-dinitronaphthalene, and 1,8-dinitronaphthalene in chloroalkanes are converted by the photochemical substitution of the nitro-groups by chlorine into the corresponding chloronaphthalenes[89]. At a concentration of 0.1 M in ethanol, 4-nitropyridine *N*-oxide is reduced to hydroxylamine[20]. Under the same conditions, at a concentration of the initial nitro-compound of 0.001 M, the nitro-group is replaced by a hydroxy-group; at moderate concentrations, the two photochemical reactions compete[20,90]. In the presence of piperidine, the substitution leads to the formation of 4-piperidinopyridine *N*-oxide[91]. The nitro-group in α-nitroazulene is readily substituted photochemically[87,92]. The photochemical substitution of the nitro-groups in certain nitrocompounds by hydroxy-groups has been discussed in a review[93].

It has been suggested that photochemical substitution takes place with participation of the triplet state[92]. This hypothesis is based on the results of experiments on the sensitisation by benzophenone of the photochemical substitution of the nitro-group in *p*-nitroanisole[94] and 2,6- and 1,7-dinitronaphthalenes[95]. The quenching of the *T* state of α-nitronaphthalene by hydroxide ions has been reported[25]; the quenching rate constant, determined from the triplet–triplet absorption spectra in degassed ethanol solutions, is 1.73×10^8 M^{-1} s^{-1}. (The quantity is equal to the sum of the rate constants for the quenching of the *T* state by hydroxide and ethoxide ions, since in ethanol solutions hydroxide ions are in equilibrium with ethoxide ions[34].)

The photochemical conversion of the nitro-group into a hydroxy-group can proceed intramolecularly via the intermediate formation of a nitrite group (the nitro–nitrite rearrangement). The nitro–nitrite rearrangement was first postulated by Chapman et al.[96] to account for the formation of anthraquinone and 10,10′-bianthrone in the photolysis of 9-nitroanthracene. They believe that the rearrangement is promoted by steric hindrance, which displaces the nitro-group from the plane of the aromatic ring. The overlap (in the excited state) of the *p*-orbital of the oxygen in the nitro-group with the *p*-orbital of the aromatic system leads to the formation of an oxaziridine ring, which is converted by a thermal reaction into a nitrite group. Other data[18,58] are consistent with this hypothesis. The hydrolysis of nitrites leads to the formation of hydroxy-derivatives, which are usually the final products of the photochemical reaction.

There are data indicating the intermediate formation of nitrites on irradiation of nitro-compounds which are not subjected to steric hindrance in the ground state. In this case, the displacement of the nitro-group from the plane of the aromatic ring is probably caused by the transition to the excited state. Thus the formation of 4-methoxy-2-nitrophenol and 3-hydroxyiminofuran-2(3*H*)-one on photolysis of *p*-nitroanisole[97] and 2-nitrofuran[98] respectively can be readily explained in terms of the nitro–nitrite rearrangement, the homolysis of the resulting nitrite into radicals, and their subsequent recombination:



The formation of 4-hydroxypyridine *N*-oxide in the photolysis of 4-nitropyridine *N*-oxide in isopropyl alcohol in the presence of HCl is explained by the intermediate rearrangement to the nitrite[90].

On photolysis of 8-nitroquinoline in benzene and alcoholic solutions, 8-hydroxyquinoline is probably formed also via the nitro-nitrite rearrangement. The intramolecular mechanism of the process is confirmed by the absence of a dependence of the quantum yield in the formation of 8-hydroxyquinoline on the concentration of hydroxide ions in the aqueous alcoholic solution and on the nature of the solvent (aqueous alcohol, benzene)[99].

It is suggested[90,97,99], that nitro-compounds are involved in this reaction in the triplet state. Thus triphenylene (E_T = 67 kcal mole^{-1}) sensitises the photochemical rearrangement of *p*-nitroanisole (E_T = 60.8 kcal mole^{-1}).[97] The conversion of 8-nitroquinoline (E_T = 58 kcal mole^{-1}) into 8-hydroxyquinoline is sensitised by benzophenone (E_T = 69 kcal mole^{-1}) and naphthalene (E_T = 61 kcal mole^{-1}).[99] Under conditions where the light flux (at a wavelength of 254 nm) is absorbed by the sensitiser ($\geq$ 90%), the quantum yield, determined from the decrease in the amount of 8-nitroquinoline, was 4.38×10^{-3} and 1.25×10^{-3} in the presence of benzophenone and naphthalene respectively. On direct excitation of 8-nitroquinoline, the yield is 1.87×10^{-3}.

VII. THE INFLUENCE OF SUBSTITUENTS AND OF THE TYPE OF THE LOWEST TRIPLET STATE ON THE PHOTOCHEMICAL REACTIVITY OF NITRO-COMPOUNDS

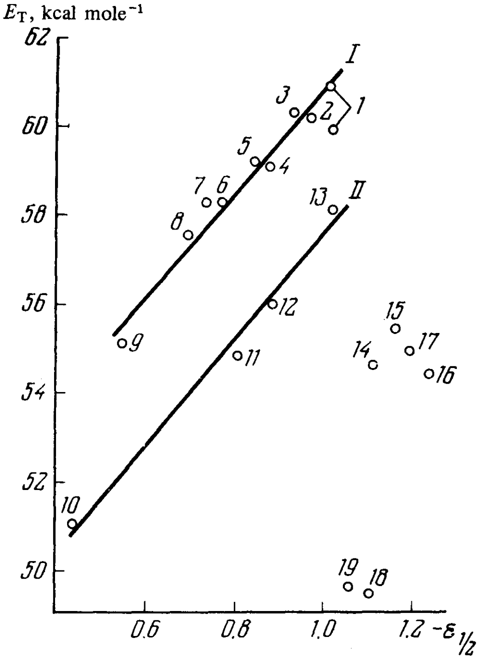
By analogy with the behaviour of ketones in photochemical reduction and on the hypothesis of the dominant role of the triplet state of nitro-compounds in these reactions, it has been suggested[82,100,101] that the reactivities of nitro-compounds in the excited state be classified in terms of their behaviour in photochemical reactions and of the type of the lowest triplet state. Nitrobenzene and its derivatives without strong electron-donating substituents are usually reduced photochemically by protic solvents. It is postulated that the reactive excited state of these compounds is of the n, π^* type[82]. The second group comprises α-nitronaphthalene and nitrobenzenes with electron-donating substituents. In the lowest excited π, π^* state, these compounds undergo photochemical substitution and reduction reactions; their ability to abstract hydrogen is diminished. Finally, the third group consists of nitro-compounds whose excited state includes a large contribution by the charge-transfer state (CTS); they are photochemically stable.

The existence of three types of nitro-compounds with different reactivities in the excited state has been confirmed by a study[101] in which a linear relation between the energy of the 0–0 transition to the triplet state and the potential of the one-electron polarographic reduction for aromatic nitrogen-compounds is reported. Similar relations have been described for aromatic hydrocarbons[102] and ketones[102–105]. In order to account for these correlations, the authors[103–105] represented the energy of excitation to the n, π^* and π, π^* triplet states by the differences between the energies of the n and π^* of the π and π^* orbitals:

$$E_T^{n\pi^*} = \varepsilon_n - \varepsilon_{\pi^*} \quad ;$$
$$E_T^{\pi\pi^*} = \varepsilon_\pi - \varepsilon_{\pi^*} \quad .$$

The introduction of substituents leads to an increase or decrease of the energy of the molecular orbital (MO). The energy of the highest occupied molecular orbital is the same for compounds of the given series (ϵ_n) or if it is linearly related to the energy of the lowest vacant molecular orbital (ϵ_{π^*}), one may expect a linear relation between the energy of the triplet state E_T and ϵ_{π^*}. Since ϵ_{π^*} varies linearly with one-electron reduction potentials[106] ($\epsilon_{1/2}$) (for nitro-compounds, this relation has been published[107]), one may expect also a linear relation between E_T and $\epsilon_{1/2}$, which is in fact the case for the various classes of compounds[101–105].

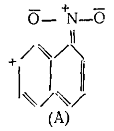
The data of Frolov et al.[101] indicate the existence of three types of relations between E_T and $\epsilon_{1/2}$ (see Figure), which corresponds to the different reactivities of nitro-compounds in the excited state: some are reduced on irradiation (the group of compounds corresponding to line I), others are difficult to reduce but undergo photochemical substitution reactions (group corresponding to line II), while unreactive compounds (nitroanilines and nitronaphthylamines) constitute an isolated group of data in the Figure.

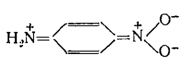


Dependence of the one-electron polarographic reduction half-wave potentials ($-\epsilon_{1/2}$, V) in dimethylformamide on the energy of the 0–0 transition to the triplet state (E_T): *1)* *p*-nitroanisole; *2)* 2-nitrobiphenyl; *3)* nitrobenzene; *4)* 2-nitrofluorene; *5)* 4-nitrobiphenyl; *6)* *m*-nitroacetophenone; *7)* 4,4′-dinitrobiphenyl; *8)* 1,8-dinitronaphthalene; *9)* 1,5-dinitronaphthalene; *10)* 1,4-dinitronaphthalene; *11)* α-nitronaphthalene; *12)* β-nitronaphthalene; *13)* 8-nitroquinoline; *14)* 4-nitrodiphenylamine; [4-nitrobiphenylylamine?]; *15)* 4-nitroaniline; *16)* *NN*-dimethyl-4-nitroaniline; *17)* 2-methyl-4-nitroaniline; *18)* 1-amino-4-nitroaniline; *19)* 2-amino-1-nitronaphthalene; E_T^I (kcal mole^{-1}) = (13.6 ± 0.9) ($-\epsilon_{1/2}$) + (47.5 ± 0.1); E_T^{II} (kcal mole^{-1}) = (12.6 ± 0.9) ($-\epsilon_{1/2}$) + (45.4 ± 0.2).

In connection with the difficulties arising in the study of the phosphorescence spectra (low-intensity structureless spectra, frequently with superposition of the luminescence of an impurity) there are relatively few data concerning the nature of the lowest triplet state of nitro-compounds[108] and those available are contradictory. Judging from the lifetime of the triplet and the fine structure of the phosphorescence spectra, nitrobenzene, 2-nitrofluorene, *p*-nitrobiphenyl, and 1,5-dinitronaphthalene[10,109] are in the *n*, π* state, while 4-nitropyridine *N*-oxide[26,110], 3- and 4-nitroquinoline *N*-oxides[110], and α- and β-nitronaphthalenes[12,23,111] are in the π, π* triplet state. These data account for lines I and II in the Figure. However, it is believed[23] that the π, π* configuration predominates in the triplet state of 1,5- and 1,8-dinitronaphthalenes.

It has also been suggested[101] that the tendency of nitro-compounds in the first group (line I in the Figure) towards reduction is due to the fact that the lowest triplet state is of the *n*, π* type (or of the π, π* type with a large *n*, π* contribution). An increase in the energy of the *n*, π* states and a decrease of the CTS level are probably characteristic of the nitro-compounds corresponding to line II in the Figure, so that there is an increase of the probability of the mixing of the lowest π, π* and CTS levels [there is an increased contribution of the type (A) structure to the triplet state]:


(A)


(B)

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An appreciable contribution of the charge-transfer state to the *T* state of α-nitronaphthalene is indicated by the marked dependence of the triplet–triplet absorption spectrum of α-nitronaphthalene on the nature of the solvent: the absorption maximum shifts from 525 nm in hexane to 580 nm in ethanol and 615 nm in *N*-methylformamide[25].

The triplet state of nitroanilines and nitronaphthylamines, constituting an isolated group, probably has the nature of an intramolecular charge transfer state [type (B)], characterised by a diminution of the electrophilic properties of the oxygen of the nitro-group as compared with the *n*, π* and π, π* states.

The different reactivities of the *n*, π, π, π*, and charge-transfer triplet states of nitro-compounds in photochemical reduction reactions can be accounted for within the framework of the usual hypotheses adopted to explain the different photochemical reactivities of the triplet states of ketones[112]: owing to the repulsion between unpaired electrons, the excited molecule resembles a "biradical" and, like all free radicals, it abstracts a hydrogen atom[113] or an electron. The electrophilic nature of such a "biradical" and hence the probability of the abstraction of a hydrogen atom (or electron) decrease on passing from the *n*, π* to the π, π* and charge-transfer states, since *n*, π* excitation entails the localisation of the positive charge on the *n* orbital of the oxygen in the nitro-group, while in the π, π* state the positive charge is delocalised over the aromatic system. Intramolecular charge transfer (CTS) leads to the localisation of a negative charge on the oxygen of the nitro-group, which reduces its electrophilic properties to an even greater extent.

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The data discussed suggest that the reduction of nitro-compounds stimulated by ultraviolet radiation is complicated by photochemical substitution processes and photochemical rearrangement of the nitro-group. The photochemical reduction of nitro-compounds in acid and alkaline media cannot be described within the framework of the photochemical dehydrogenation mechanism, since the quantum yield of the reaction in acid and alkaline media depends on the concentration of the acid or the alkaline reagent.

A number of problems arising in the study of the photochemical reactions of nitro-compounds have not been elucidated. Thus the available data permit only hypotheses concerning the changes in mechanism in the primary photochemical reduction step on passing from neutral to acid and alkaline media. The nature of the intermediate species in these processes is not clear. The data described are consistent with the orthodox view[1] concerning the dominant role of the triplet state of nitro-compounds in photochemical reduction reactions. With the exception of the study of Capellos and Porter[25], there is no direct evidence for the involvement of the triplet state of nitro-compounds in the reaction. The participation of the excited singlet state of nitro-compounds in the reactions considered has not been disproved experimentally.

The first attempts have been made to explain the influence of substrate structure on the photochemical reactivity of the nitro-group by a change in the nature of the reactive *T* state of nitro-compounds. Systematic studies of the influence of the structure of nitro-compounds on the competition of photochemical reduction and substitution processes and the nitro–nitrite rearrangement have not been made.

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Dithiocarboxylic Acids, Their Esters, and Metal Dithiocarboxylates

E.Jansons

The present state of the chemistry of dithiocarboxylic acids is described and methods for the synthesis of both the acids themselves and their esters and metal dithiocarboxylates are discussed. Data are presented on the properties and applications of these substances.

The bibliography includes 350 references.

CONTENTS

I. INTRODUCTION

By analogy with the carboxy-group COOH, the sulphur-containing functional group CSSH is called the dithiocarboxy-group. For this reason, the compounds R-CSSH, in which the organic moiety is linked to the dithiocarboxy-group by a carbon–carbon bond, should be called dithiocarboxylic acids. This term is in fact used in the English and American chemical literature†.

The names of the individual examples of compounds of this class are devised in accordance with the principles of the IUPAC nomenclature on the basis of the name of the corresponding hydrocarbon.

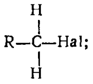
The first example of dithiocarboxylic acids (C_6H_5CSSH) was synthesised more than 100 years ago in 1866[1]. However, due attention was not devoted to compounds of this class for a long time. This can be apparently partly accounted for by the low stability in air of many dithiocarboxylic acids and partly by the unpleasant smell of these substances (particularly the alkyl derivatives) which has been very strikingly described by the first investigators[2].

The chemistry of dithiocarboxylic acids began to develop vigorously in the 1960's. During the last 6–7 years, approximately as many studies have been published as during the previous 100 years. Certain reviews have also been published[3-6], but these do not cover all the aspects of the chemistry of dithiocarboxylic acids. The present paper surveys the literature on dithiocarboxylic acids, their esters, and metal dithiocarboxylates up to 1973 (and partly also 1974).

II. METHODS FOR THE SYNTHESIS OF DITHIOCARBOXYLIC ACIDS

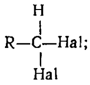
1. Synthesis from Compounds Containing a Halogenomethyl Group

Compounds containing mono-, di-, and tri-halogenomethyl groups may be used as the starting materials of the synthesis of dithiocarboxylic acids:



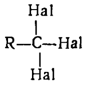
$R{-}CH_2{-}Hal$;

(I)



$R{-}CH(Hal){-}Hal$;

(II)



$R{-}C(Hal)_2{-}Hal$,

(III)

where R is an organic group and Hal a halogen. Compounds (III) can also be used in syntheses with R = H. In all cases, the syntheses are carried out in alcoholic solutions.

The monohalogeno-derivatives (I) react with finely dispersed sulphur in the presence of alkali metal alkoxides. The alkoxide ion, being a strong base, cleaves the eight-membered ring of the sulphur molecule under these conditions[7,8] and gives rise to the chemically highly reactive ion $CH_3O{-}S{-}S_6{-}S^-$, which reacts with the monohalogeno-derivative (I). The dithiocarboxylic acids are synthesised in accordance with the following overall equation:

$$R{-}CH_2Hal + 2S + 2NaOCH_3 \rightarrow R{-}CSSNa + NaHal + 2CH_3OH.$$

After the solution has been acidified, the corresponding dithiocarboxylic acid is isolated. Benzenedithiocarboxylic, 4-chlorobenzenedithiocarboxylic, and 2,6-dichlorobenzenedithiocarboxylic acids have been obtained by this method in methanol solutions[7,9,10].

On interaction with ethanol solutions of KHS, the dihalogeno-derivatives (II) give rise to the corresponding potassium dithiocarboxylates as side products in addition to the disulphide[1,11]:

$$3R{-}CHHal_2 + 7KHS \rightarrow (R{-}CH_2S)_2 + R{-}CSSK + 3H_2S + 6KHal.$$

This method is also of historical importance—it was in fact used to synthesise the first dithiocarboxylic acid[1].

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†The following section of the original Russian text has been omitted here. However, in the Russian literature compounds containing the carboxy-group are traditionally called carbonic acids and in the present paper the term "dithiocarbonic acids" is used instead of the systematic term "dithiocarboxylic acids".

The trihalogeno-derivatives (III) can be converted into dithiocarboxylate ions by treatment with alkali metal sulphides, hydrogen sulphides, or trithiocarbonates in ethanol or methanol solutions:

$$\mathrm{R{-}CHal_3 + 2K_2S \rightarrow R{-}CSSK + 3KHal;}$$
$$\mathrm{R{-}CHal_3 + 4KHS \rightarrow R{-}CSSK + 3KHal + 2H_2S;}$$
$$\mathrm{R{-}CHal_3 + 2Na_2CS_3 \rightarrow R{-}CSSNa + 3NaHal + 2CS_2.}$$

On subsequent acidification, the corresponding dithiocarboxylic acids are isolated in a free form. The rapidly polymerising dithiocarboxylic acid HCSSH was obtained by this procedure from chloroform and potassium sulphide in ethanol solution[12-14]. It can be obtained in a purer form by carrying out the synthesis in the absence of air and in methanol solutions[15,16].

$C_6H_5CCl_3$ can be converted into benzenedithiocarboxylic acid by treatment with potassium sulphide[17,18] or hydrogen sulphide[19] in ethanol solutions and by potassium sulphide in methanol solution[20]. When sodium trithiocarbonate is used[21,22], the synthesis is carried out in aqueous methanol solution.

Chlorobenzenedithiocarboxylic[17], pyridine-4-dithiocarboxylic[23], quinoline-2-dithiocarboxylic, and quinoline-4-dithiocarboxylic[24] acids have been obtained similarly.

2. Interaction of Organometallic Compounds with Carbon Disulphide.

The first attempts to obtain dithiocarboxylic acids by the interaction of carbon disulphide with organosodium and organozinc compounds were unsuccessful[25]. When triethylaluminium was used, only traces of ethanedithiocarboxylic acid were obtained[26]. Later it was shown that organolithium and organosodium compounds can be used successfully to synthesise dithiocarboxylic acids[27,28]. The reactions with carbon disulphide were then carried out in ethyl ether solutions in an atmosphere of nitrogen:

$$\mathrm{R{-}Me + CS_2 \rightarrow R{-}CSSMe.}$$

Lithium naphthalene-1-dithiocarboxylate $C_{10}H_7CSSLi$ and sodium diphenylmethanedithiocarboxylate $(C_6H_5)_2CHCSSNa$ were obtained in this way.

Organomagnesium compounds have found the widest applications in the synthesis of dithiocarboxylic acids and were proposed for this purpose at the beginning of the century[2,29-32]. Here the starting materials are the corresponding halogeno-derivatives, which react with metallic magnesium in an ethereal medium:

$$\mathrm{R{-}Hal + Mg \rightarrow R{-}MgHal.}$$

Some workers recommend that this reaction be carried out in the absence of air, for example, in an atmosphere of nitrogen[33]. The addition of carbon disulphide to a solution of organomagnesium compound results in the formation of dithiocarboxylates:

$$\mathrm{R{-}MgHal + CS_2 \rightarrow R{-}CSSMgHal.}$$

The dithiocarboxylic acids can be isolated in a free state by treating the reaction mixture with hydrochloric acid.

The diethers of poly(ethylene glycols) have also been proposed as solvents instead of ethyl ether. For example, pyridine-2-dithiocarboxylic acid has been obtained[34] in solution of the dimethyl ether of diethylene glycol. The synthesis can also be achieved in tetrahydrofuran[24].

Organomagnesium compounds have been used to synthesise the following dithiocarboxylic acids: methanedithiocarboxylic[32,35], ethanedithiocarboxylic[2], propanedithiocarboxylic[2], 2-methylpropanedithiocarboxylic[2], 3-methylbutanedithiocarboxylic[2], cyclohexanedithiocarboxylic[36], phenylmethanedithiocarboxylic[29,30,37], hydropinenedithiocarboxylic[31], benzenedithiocarboxylic[18,30,33,38-43], 2-methylbenzenedithiocarboxylic[33,41], 4-methylbenzenedithiocarboxylic[33,41,44,45], 4-chlorobenzenedithiocarboxylic[41,44], 4-bromobenzenedithiocarboxylic[30,47], 5-isopropyl-2-methylbenzenedithiocarboxylic[48], naphthalene-1-dithiocarboxylic[30,33,39,41,49], naphthalene-2-dithiocarboxylic[41,47,50], pyrroledithiocarboxylic[41,51-53], indole-3-dithiocarboxylic[41,52,53], 2-methylindole-3-dithiocarboxylic[52], pyridine-2-dithiocarboxylic[34], quinoline-2-dithiocarboxylic[24], and thiophen-2-dithiocarboxylic[41]. Alkanedithiocarboxylic acids are obtained by this procedure in very low yields (5–25%). The yields of compounds with aromatic groups are very much higher (usually between 40% and 80%) (see also Ref. 54).

3. Interaction of Aldehydes with Hydrogen and Ammonium Polysulphides

Aromatic aldehydes and hydrogen polysulphide form brownish-yellow or reddish resinous products in the presence of condensing agents such as zinc chloride, hydrogen chloride, sulphuric acid, etc. The products are ground and treated with an aqueous or alcoholic solution of KOH and the insoluble residues are filtered off. The filtrate consists of a solution of the corresponding potassium dithiocarboxylate[55-57]. The following dithiocarboxylic acids have been synthesised by this method: benzenedithiocarboxylic[57], 2-hydroxybenzenedithiocarboxylic[55,57], 2- and 4-methoxybenzenedithiocarboxylic[55,57], and furan-2-dithiocarboxylic[58].

The method has not found more extensive applications probably for the simple reason that dithiocarboxylic acids can be obtained from aldehydes more conveniently by the reaction of the latter with ammonium polysulphide. This reaction was used for the first time to synthesise benzenedithiocarboxylic acid[59]. A concentrated solution of ammonia and copper powder was added to an ethanol solution of benzaldehyde, after which the latter was saturated with hydrogen sulphide. Later it was suggested that ammonium polysulphide be prepared beforehand. Dithiocarboxylic acids are synthesised by adding the solution to an aldehyde or to an ethanol solution of an aldehyde[58,60]:

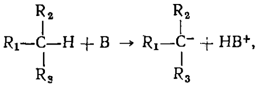
$$\mathrm{R{-}CHO + (NH_4)_2S_2 \rightarrow R{-}CSSNH_4 + NH_4OH.}$$

After acidification with hydrochloric acid, the free dithiocarboxylic acids are obtained.

The following dithiocarboxylic acids have been synthesised by this method: benzenedithiocarboxylic[45,58], 2-chlorobenzenedithiocarboxylic[41,45], 4-chlorobenzenedithiocarboxylic[45], 2-hydroxybenzenedithiocarboxylic[41,45,58,61,62], 4-hydroxybenzenedithiocarboxylic[41,45], 4-methoxybenzenedithiocarboxylic[41,45,58,61,62]; 3,4-dihydroxybenzenedithiocarboxylic[61,62], 4-hydroxy-3-methoxybenzenedithiocarboxylic[45,58,61,62], 3,4-methylenedioxybenzenedithiocarboxylic[45,58,61,62], 4-aminobenzenedithiocarboxylic[45], 4-dimethylaminobenzenedithiocarboxylic[45], 4-acetamidobenzenedithiocarboxylic[41], 3-sulphobenzenedithiocarboxylic[63], 4-hydroxy-3-sulphobenzenedithiocarboxylic[63], 1-phenylethylene-2-dithiocarboxylic[62], naphthalene-2-dithiocarboxylic[64], furan-2-dithiocarboxylic[42,58,61,62,65], and thiophen-2-dithiocarboxylic[41]. The yields are usually between 20 and 45%.

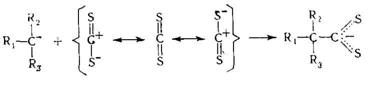
4. Reactions of CH acids with Carbon Disulphide (with Xanthates and Trithiocarbonates)

In the presence of a sufficiently strong base, CH acids react with carbon disulphide to form dithiocarboxylate ions. It is suggested that the reaction proceeds via a mechanism[66-69] which begins with a protolytic reaction:

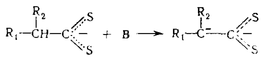


$$R_1-\overset{R_2}{\underset{R_3}{C}}-H + B \rightarrow R_1-\overset{R_2}{\underset{R_3}{C^-}} + HB^+,$$

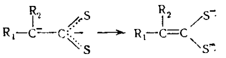
where B is the base and HB^+ the conjugate acid. This is followed by the electrophilic addition of carbon disulphide via its carbon atom to the base (carbanion) $R_1R_2R_3C^-$:



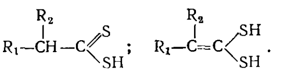
If the initial compound with $R_3 = H$ contains an activated methylene group $R_1R_2CH_2$, then substances of this kind initially react only via the mechanism described above, which results in the formation of $R_1R_2CH-CSS^-$. However, when the dithiocarboxylate ion is still a fairly strong CH acid, the following protolytic reaction takes place:



The subsequent redistribution of charges in such cases yields the dianions of ene-1,1-dithiols:



Here one must note that the treatment of ene-1,1-dithiolate ions with acids can lead to their reconversion into dithiocarboxylate ions[70]. The dithiocarboxylic acids themselves and the ene-1,1-dithiols are isomers:

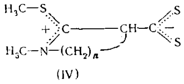


It follows from the foregoing that, in those cases where $R_3 = H$ (or $R_3 = R_2 = H$) in the initial compound dithiocarboxylic acids can occur in the synthesis only as intermediates.

NaOH, KOH, alkoxides [CH_3ONa, C_2H_5ONa, $(CH_3)_3CONa$, and $(CH_3)_2(C_2H_5)CONa$], sodamide ($NaNH_2$), sodium hydride (NaH), and in some cases even metallic sodium are used as bases. Ammonia in the form of a concentrated aqueous solution or in the liquid state sometimes plays the role of this component. Depending on the properties of the reactants, the solvents may be hydrocarbons (pentane, benzene), alcohols (methanol, ethanol), ethers (ethyl ether, dioxan, tetrahydrofuran), acetone, acetonitrile, dimethyl sulphoxide, dimethylformamide, and dimethylacetamide.

Many dithiocarboxylic acids or the corresponding ene-1,1-dithiols have been synthesised by the above method. The starting materials in these processes were aldehydes ($R_1 = CHO$, $R_3 = H$)[71], ketones ($R_1 = RCO$, $R_3 = H$)[38,72-85], nitromethane ($R_1 = NO_2$, $R_2 = R_3 = H$)[86-88], phenols, naphthols, hydroxyquinoline[67,89-91], malonic acid derivatives ($R_3 = H$)[69,76,82,92-101], pyrrole, pyridine, indole, quinoline, and their derivatives[76,102-108], ketimines of cyclohexanone and cyclopentanone [$R_2 = -(CH_2)_n-\underset{|}{C}=N-R$, $R_3 = H$][109,110], compounds with the sulphonyl group ($R_1 = RSO_2$, $R_3 = H$)[111], sodium cyclopentadienide (R_1R_2 = cyclopentadienide ion, $R_3 = H$)[112,113], and pyrazolone derivatives (R_1R_2 = the residue of pyrazolone derivative, $R_3 = H$).[114-116]

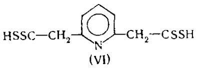
Dithiocarboxylic acids have been obtained by this method also in the reaction of carbon disulphide with the Reissert compound[117], with dinitrotoluene[76], and with the quaternary salts derived from heterocyclic nitrogen compounds[118,119]. Dithiocarboxylic acids which are stable dipoles of type (IV)[120,121], and even the bisdithiocarboxylic acids (V)[122] and (VI)[76] have also been obtained:



(IV)

HSSC—CH₂—CO—CH₂—CSSH

(V)

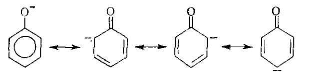


(VI)

A variety of the above method for the synthesis of dithiocarboxylic acids is that consisting of heating phenols with alkali metal xanthates or trithiocarbonates. On increase of temperature, these reactants decompose into carbon disulphide and the alkoxide (sulphide):

$$C_2H_5-O-CSSK \rightarrow CS_2 + C_2H_5OK;$$
$$Na_2CS_3 \rightarrow CS_2 + Na_2S.$$

Alkoxide or sulphide ions play the role of a strong base, the presence of which is necessary for reaction with carbon disulphide. The site of addition of carbon disulphide is determined under these conditions by the existing resonance or tautomeric forms of the corresponding phenoxide ion, for example:

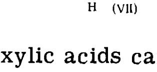


Evidently the addition should take place in the *ortho*- or *para*-positions.

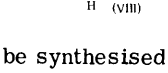
The following dithiocarboxylic acids have been obtained by this method: 4-hydroxybenzenedithiocarboxylic[123], 2,4-dihydroxybenzenedithiocarboxylic[124-127], 2-4-dihydroxy-6-methylbenzenedithiocarboxylic[123], 2,3,4- and 2,4,6-trihydroxybenzenedithiocarboxylic[125,127], 1-hydroxynaphthalene-2-dithiocarboxylic[128], and 8-hydroxyquinoline-7-dithiocarboxylic[124]. The method of synthesis using a xanthate suffers from the disadvantage that the syntheses must be performed at high temperatures and pressures.

5. Other Methods for the Synthesis of Dithiocarboxylic Acids

Under the conditions of the Friedel-Crafts synthesis (with anhydrous aluminium chloride as the catalyst), pyrrole derivatives react with carbon disulphide. The acids (VII) and (VIII) have been obtained in this way[129]:



(VII)

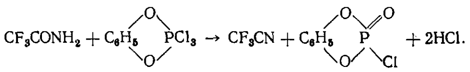


(VIII)

Dithiocarboxylic acids can be synthesised by hydrolysing their esters. Ethane-, methane-, benzene-, 4-methylbenzene-, and phenylmethane-dithiocarboxylic acids as well as HSSC-CSSH have been obtained by treating the corresponding esters with alcoholic KOH solution[130]. 3-Antipyrine-4-dithiocarboxylic acid was obtained after heating its ethyl ester for 1 h on a water bath with a 10% alcoholic KOH solution[131]. The 4-dithiocarboxylic acids of antipyrine[132] and isoantipyrine[133] have been prepared by heating their ethyl esters with an ethanol solution of KHS

(1–2 h, on a water bath). In order to obtain benzenedithiocarboxylic acid, its methyl ester was hydrolysed overnight at room temperature with NaHS solution[134].

Trifluoromethanedithiocarboxylic acid has been synthesised from trifluoroacetamide, which was initially converted into the nitrile by treatment with 1,2-phenylenedioxyphosphorus trichloride[135]:



The nitrile was then thiolysed[136,137] with a mixture of liquid H_2S and HCl (40°C, 28 atm, 2–3 days):

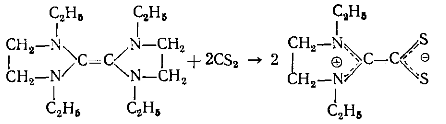
$$CF_3CN + H_2S \rightarrow CF_3CSNH_2;$$
$$CF_3CSNH_2 + H_2S + HCl \rightarrow CF_3CSSH + NH_4Cl.$$

Cyanodithioformate ions are formed[138,139] when cyanide ions interact with carbon disulphide in a dimethylformamide solution:

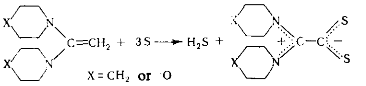
$$CN^- + CS_2 \rightarrow NC\text{—}CSS^-.$$

Cyanodithioformic acid $(NCCSSH)_X$ is obtained by the subsequent addition of concentrated hydrochloric acid.

The synthesis of dithiocarboxylic acids derived from peraminoethylenes is very unusual[140]. The reaction takes place exothermically with 98% yield in accordance with the following equation:



Analogous zwitter-ions were obtained[141] as a result of the interaction of certain compounds containing an active methylene group with elemental sulphur:



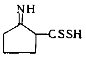
X = CH$_2$ or O ;

III. THE PROPERTIES AND APPLICATIONS OF DITHIOCARBOXYLIC ACIDS

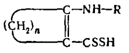
1. Physical properties

Dithioformic and cyanodithioformic acids are weakly coloured polymeric substances[13,14,16,138,139,142]. The radius of the dithioformate ion has been calculated from the measured conductivities of the solutions[143].

Aliphatic dithiocarboxylic acids as well as phenylmethanedithiocarboxylic acids are orange oily liquids[2,30,32,130]. This is also true of trifluoromethanedithiocarboxylic acid[136,137]. Cyclohexanedithiocarboxylic acid is a reddish-brown liquid[36]. The dithiocarboxylic acids obtained from iminopentane (IX)[84] and its derivatives[85] and also from cyclopentene and cyclohexene (X) derivatives[109] are crystalline substances melting between 66° and 117°C:



(IX)



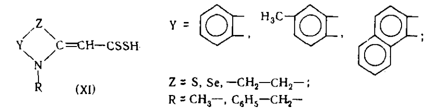
(X)

$n = 3; 4$.

Benzenedithiocarboxylic acid and its halogeno-, methyl, and isopropyl derivatives are red or red-violet oily liquids[1,30,38,44,48,55,57,130]. 4-Hydroxy- and 3,4-dihydroxybenzenedithiocarboxylic acids are likewise oily liquids[62,123,144]. 2-Hydroxy- and 2,4-dihydroxybenzenedithiocarboxylic acids have been obtained in the form of a thick, red, rapidly solidifying mass[144,145]. The latter acid forms a yellow crystalline monohydrate[125,126,146]. 2,3,4-Trihydroxy-[125,128], 4-methoxy-[55,57,62], 4-hydroxy-3-methoxy-[62,147], 3,4-methylenedioxy-[62,148], and 4-hydroxy-3-sulpho-benzenedithiocarboxylic[63] acids are likewise crystalline. Naphthalene-1- and naphthalene-2-dithiocarboxylic acids are dark-red oily liquids[30,33,149,150], while 1-hydroxynaphthalene-2-dithiocarboxylic acid is a dark-yellow crystalline substance[89,128].

Furan-2-[62,65,148], pyrrole-2-[51,52], and indole-3-dithiocarboxylic[52] acids are red oily liquids but the dithiocarboxylic acids obtained from certain pyrrole[108], indole[104], pyridine[103], and quinoline[102] derivatives are crystalline substances. Dithiocarboxylic acids of type (XI) are yellow crystalline substances (m.p. between 200° and 288°C)[119] like the dithiocarboxylic acids obtained from pyrazolone derivatives (m.p. between 115° and 230°C)[114–116,132].

Zwitter-ionic dithiocarboxylic acid has been obtained in the form of dark-red substances melting at 178–179°C[140] and 233–236°C[141]:



Y = ;

Z = S, Se, —CH$_2$—CH$_2$—;

R = CH$_3$—, C$_6$H$_5$—CH$_2$— .

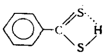
Dithiocarboxylic acids are sparingly soluble in water, dissolving more or less readily in organic solvents.

2. Absorption Spectra

The electronic absorption spectra of dithiocarboxylic acids differ little from those of their esters[151,152]. The electronic absorption spectra of methane-[152], ethane-[153], cyclohexane-[154], phenylmethane-[155,156], benzene-[152,156,157], 4-chlorobenzene-[157], 4-methylbenzene-[158], 2-hydroxybenzene-[145], 4-hydroxybenzene-[144,159], 2,4-dihydroxybenzene-[144,146], 2,3,4-trihydroxybenzene[144], 4-hydroxy-3-methoxybenzene-[147], naphthalene-1- and naphthalene-2-[150], pyrrole- and indole-[160,161], and quinoline-2- and quinoline-4-dithiocarboxylic[162] acids are available in the literature. Other publications quote only numerical data characterising the absorption maxima (wavelengths and molar extinction coefficients). Such data are available for methane-, trimethylmethane-, phenylmethane-, benzene- and 4-methylbenzene-dithiocarboxylic acids[163], for acids (IX)[85] and (X)[109], and for zwitter-ionic dithiocarboxylic acids.

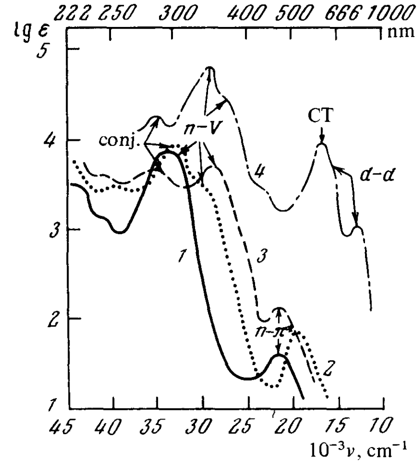
The absorption bands in the electronic spectra of phenylmethane- and benzene-dithiocarboxylic acids have been assigned[156] (see Figure).

The low-intensity band ($\epsilon < 100$) observed in the visible spectra has been assigned to $n-\pi^*$ transitions. Resolution of this band in the absorption spectrum of benzenedithiocarboxylic acid into two components led to the conclusion that there is a hydrogen bond in the dithiocarboxy-group, as in formula (XII)[164]; the energy of this bond is 4.5 ± 0.5 kcal mole^{-1}:



(XII) .

The ultraviolet spectra of phenylmethane- and benzenedithiocarboxylic acids as well as the spectra of the corresponding anions (see Figure) contain a high-intensity band, which has been assigned to $n-V$ transitions[156]. In the spectra of benzenedithiocarboxylic acid and its anion, there is a second high-intensity absorption band, which has been assigned to $\pi-\pi^*$ transitions in the conjugated system of the benzene ring with the dithiocarboxy-group (in the Figure, it is designated by "conj."). These absorption band assignments were extended also 4-chloro- and 4-methyl-benzenedithiocarboxylic acids[165].



Electronic absorption spectra: 1) phenylmethanedithiocarboxylic acid in carbon tetrachloride; 2) benzenedithiocarboxylic acid in ethyl ether; 3) benzenedithiocarboxylic acid in water; 4) nickel benzenedithiocarboxylate in chloroform[157].

Vibrational spectra. A spectrum in the range 526–4000 cm^{-1} was obtained[142] for the dithioformic acid trimer $(HCSSH)_3$. There are numerical data for the same part of the spectrum of the polymeric acid $(HCSSH)_x$.[16,142] The absorption at 2500 cm^{-1} has been assigned to ν(S–H) and that at 1166 and 1048 cm^{-1} to the stretching and deformation vibrations of the CSC group.

The spectrum of cyanodithioformic acid $(NC{-}CSSH)_x$ was recorded in the range 526–4000 cm^{-1}.[166] The (C≡N) band was found at 2250 cm^{-1}, which led to the conclusion that the polymerisation of this acid as well as that of dithioformic acid involves the C=S group.

The spectra of liquid (400–10 000 cm^{-1}) and gaseous (750–10 000 cm^{-1}) methanedithiocarboxylic acid have been obtained[167] and the following assignments of the absorption wavenumbers have been made: 2481 cm^{-1} to ν(SH), 1216 cm^{-1} to ν(C=S), 581 cm^{-1} to ν(C–S) and 860 cm^{-1} tentatively to δ(SH). Calculation of the normal vibration wavenumbers for this acid on a computer[168] led to the following assignments:

2976 cm^{-1} to CH stretch.;
2918 cm^{-1} to CH stretch.;
2481 cm^{-1} to SH stretch.;
1431 cm^{-1} to CH def.;
1357 cm^{-1} to CC stretch. + CH def.;
$\left\{\begin{matrix}1192\\1216\end{matrix}\right.$ cm^{-1} to CC stretch. + SCC def. + SCS def. + CH def.;
$\left\{\begin{matrix}1072\\1107\end{matrix}\right.$ cm^{-1} to SCC def. + SCS def. + SH def.;
903 cm^{-1} to CC stretch.+ CS stretch.+ SH def.;
$\left\{\begin{matrix}860\\873\end{matrix}\right.$ cm^{-1} to CS stretch. + CH def.;
581 cm^{-1} to CS stretch.;
406 cm^{-1} to CCS def.

The spectra of solutions of trifluoromethanedithiocarboxylic acid in carbon tetrachloride and in carbon disulphide have been obtained (670–4000 cm^{-1})[169] as well as numerical data for the absorption wavenumbers[136,137,169]. The following assignments have been made:

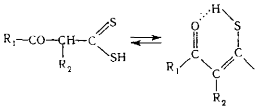
2577-2580 cm^{-1} to ν(SH);
1253 cm^{-1} to $\nu_{asym}(CS_2)$;
933-945 cm^{-1} to δ(SH)?
690-691 cm^{-1} to $\nu_{sym}(CS_2)$.

The vibrational spectrum of benzenedithiocarboxylic acid[20] contains intense absorption bands at 1690 and 1270 cm^{-1}. The shift of ν(SH) on passing from the spectrum of its 20% solution in carbon tetrachloride indicates[170] the existence of the hydrogen bond S–H...S [see also formula (XII)].

The vibrational absorption spectra of 2-hydroxy-[145], 4-hydroxy-[123], and 2,4-dihydroxy-benzenedithiocarboxylic[123,146] acids have likewise been published. The following assignments have been made for the last acid[146]: 2530 cm^{-1} to ν(SH); 1250–1240 cm^{-1} to δ(OH), ν(C=S)?; 685 cm^{-1} to ν(C–S)? The study of the spectrum of 2-hydroxybenzenedithiocarboxylic acid led to the conclusion that there is an intramolecular hydrogen bond in this compound[145].

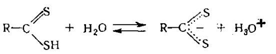
3. Chemical Properties

There may be a tautomeric equilibrium between dithiocarboxylic acids and the corresponding ene-1,1-dithiols. The equilibrium has been detected[171] in the dithiocarboxylic acids obtained by the reaction between carbon disulphide and ketones:



.

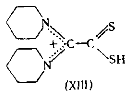
Dithiocarboxylic acids enter into a protolytic interaction with water molecules:



$$R{-}C(=S)SH + H_2O \rightleftharpoons R{-}CS_2^- + H_3O^+$$

.

In an alkaline medium, where hydronium ions combine with hydroxide ions, the dithiocarboxylic acids, which are sparingly soluble in water, therefore dissolve in the form of dithiocarboxylate ions:



(XIII)

.

The strongest dithiocarboxylic acid is compound (XIII) ($pK_a \simeq -2$).[141] The pK_a values for other dithiocarboxylic acids vary in the range from 1 to 3 (see Table). $pK_1 < 2$ and $pK_2 \simeq 5.2$ have been found for nitromethanedithiocarboxylic acid[88] (pK_2 corresponds to the second dissociation involving the conversion of the dithiocarboxylate ion into the ene-1,1-dithiolate ion).

Dithiocarboxylic acids are extremely reactive. They undergo intense colour reactions with textiles and form dark stains on leather[30,32,172]. On storage, many dithiocarboxylic acids decompose rapidly or are oxidised. For example, an ethereal solution of benzenedithiocarboxylic acid may be stored without significant changes for more than 1 h only in an atmosphere of an inert gas[172]. This by no means applies to all dithiocarboxylic acids. There are also extremely stable representatives of compounds of this class, for example the dithiocarboxylic acids obtained from derivatives of pyrazolone[114-116, 132], 4-hydroxy-3-methoxybenzenedithiocarboxylic acid[147], and the acids (X), (XI), and (XII).

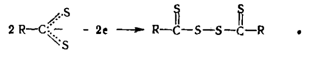
The pK_a values for dithiocarboxylic acids in aqueous solutions.

No.	Acid	pK_a	References
1	Dithioformic	0.85	143
2	Methanedithiocarboxylic	2.55	152
3	Ethanedithiocarboxylic	2.65±0.05	153
4	1-Oxopropanedithiocarboxylic	2.15	77
5	Phenylmethanedithiocarboxylic	2.05±0.04	155
6	Benzenedithiocarboxylic	1.92±0.06	157
7	4-Chlorobenzenedithiocarboxylic	1.7	157
8	4-Methylbenzenedithiocarboxylic	2.3	157
9	2-Hydroxybenzenedithiocarboxylic	1.60±0.06	145
10	4-Hydroxybenzenedithiocarboxylic	2.58±0.07	144
11	2,4-Dihydroxybenzenedithiocarboxylic	1.91±0.08	144
12	2,3,4-Trihydroxybenzenedithiocarboxylic	1.72±0.04	144
13	3,4-Methylenedioxybenzenedithiocarboxylic	2.29±0.07	148
14	Furan-2-dithiocarboxylic	2.04±0.04	148

When nitromethane-[86], 2,4-dihydroxybenzene-[124, 126], 2,3,4-trihydroxybenzene[125], and 1-hydroxynaphthalene-2-dithiocarboxylic[128] acids are heated with concentrated aqueous solutions of alkalis, sulphur is split off and the corresponding carboxylic acids are formed.

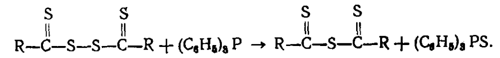
The reducing action of amalgamated zinc on benzene-, 4-methoxybenzene-, and phenylmethane-dithiocarboxylic acids has been investigated in hydrochloric acid solutions. Under these conditions, benzenedithiocarboxylic acid is largely converted after interaction for 10 min into phenylmethanethiol ($C_6H_5CH_2SH$) (yield 25%); stilbene and benzoic acids are also formed and a considerable proportion of the substance char. When the above three dithiocarboxylic acids are reduced polarographically, three waves are observed in each individual instance. The first corresponds to the reduction of the disulphide formed in the solution of the supporting electrolyte, the second to the reduction of the thiocarbonyl group, and the third to the reduction of the dithiocarboxylate ion[54].

When cyclohexane-[36], 4-methylbenzene-[44], and 8-hydroxyquinoline-7-dithiocarboxylic[124] acids are treated with strong oxidising agents ($KMnO_4$, HNO_3), the corresponding carboxylic acids are formed. On oxidation of alkali metal dithiocarboxylates under milder conditions (with iodine, hydrogen peroxide, and atmospheric oxygen), the products are usually disulphides, which precipitate:



The disulphides containing aliphatic groups are as a rule yellow, while those containing aromatic and heterocyclic groups are red. Dithioformic acid gives rise to a polymeric disulphide[12, 173].

Disulphides can be converted into monosulphides by treatment with triphenylphosphine[174]:



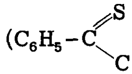
$$R-\overset{\overset{\displaystyle S}{\|}}{C}-S-S-\overset{\overset{\displaystyle S}{\|}}{C}-R+(C_6H_5)_3P \rightarrow R-\overset{\overset{\displaystyle S}{\|}}{C}-S-\overset{\overset{\displaystyle S}{\|}}{C}-R+(C_6H_5)_3PS.$$

A solution of bis-(1-thionaphthoyl) disulphide in fused naphthalene exhibits thermochromic properties, i.e. the colour of the solution changes as the temperature is altered[175,176]. This is explained by the formation of free radicals:

$$C_{10}H_7-CS-S-S-CS-C_{10}H_7 \rightleftarrows 2C_{10}H_7-CS-S^{\cdot}.$$

A 0.005% benzene solution or a 0.05% chloroform solution of bis-(2-hydroxythiobenzoyl) disulphide have been suggested as reagents for the extraction-colorimetric determination of microgram amounts of nickel[177].

Dithiocarboxylic acids react with ammonia derivatives such as amines, hydroxylamine, hydrazine, and semicarbazide. The reaction with primary amines $R'NH_2$ yields the corresponding thioamides RCSNHR'. This has been used for the thioacylation of uracil and pyrimidine derivatives[178]. The corresponding derivatives of dithiocarboxylic acid obtained from pyrazolones[114,115,131] and the acids $RCOCH_2CSSH$ have also been synthesised[179,180]. As a result of interaction with dithiocarboxylic acids, 1,2-phenylenediamine yields substituted benzimidazoles[181]. In the presence of an oxidising agent (elemental iodine), dithiocarboxylic acids react with cyclohexylamine and the products are again thioamides[39,182]. The reaction of aromatic dithiocarboxylic acids with hydroxylamine gives rise to the oximes RCH=NOH,[46, 183] while the reaction between hydroxylamine and non-aromatic dithiocarboxylic acids gives rise to the nitriles RCN.[183] Aromatic dithiocarboxylic acids react with hydrazine to form the hydrazones $RCH{=}NNH_2$ and the reactions with methyl-, phenyl-, and methylphenyl-hydrazines result in the formation of the corresponding substituted hydrazones[23,48,114,183-186]. Aliphatic dithiocarboxylic acids react with these reagents to form the thiohydrazides $RCSNHNH_2$. The reaction between semicarbazide and aromatic dithiocarboxylic acids leads to the formation of the semicarbazones $RCH{=}NNHCONH_2$.[47,183]

Benzenedithiocarboxylic acid reacts with thionyl chloride ($SOCl_2$) to form[38, 43, 134] thiobenzoyl chloride  . 4-Methyl-, 3-chloro-, 4-chloro-, and 4-methoxy-benzenedithiocarboxylic acids as well as thiophen-2-dithiocarboxylic acid react similarly[187].

4. Applications of Dithiocarboxylic Acids

Dithiocarboxylic acids can be used in organic synthesis as thioacylating agents. Their reactions with azolides constitute the basis of one of the methods for the synthesis of thioamides[188]. Substituted methane dithiocarboxylic acids can serve as the starting materials for the synthesis of compounds with sulphur-containing rings[189].

Dithioformic acid has been used as a reagent for the introduction of sulphur into proteins[190]. Various dithiocarboxylic acids have been suggested as effective agents accelerating the vulcanisation of raw rubber[58,60,61,191]. Copolymerisation with benzenedithiocarboxylic acid makes it possible to increase the elasticity and to improve other properties of many polymers[192,193]. Hydroxy-derivatives of benzenedithiocarboxylic acid exhibit bactericidal and fungicidal properties and can find appropriate applications[91].

IV. DITHIOCARBOXYLIC ACID ESTERS

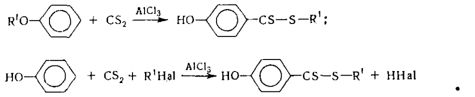
1. Methods of Synthesis

The esters can be obtained from the corresponding dithiocarboxylic acids. Historically, this is the first method for the synthesis of the esters, but it is still used on a fairly large scale. The esters are sometimes obtained by alkylating the dithiocarboxylic acids themselves [109, 119], but normally their salts are used for this purpose: the sodium [41,44,48,54,79,194-197], potassium [13, 18,19,24,57,82,115,116, 132,144,198-200], silver [57], ammonium [146,201], and magnesium halide salts RCSSMgHal, obtained in the synthesis of dithiocarboxylic acids using organomagnesium compounds [37,40,202,205]. The zwitter-ionic dithiocarboxylic acids react directly with methyl iodide [121,141]. Dimethyl sulphate [44,48,54,57,66,82,108,109,115,116,119,132,144,195,197,199,202,203,205], diethyl sulphate [24,108,203,204], methyl iodide [13,121,141,146,196, 200,206], ethyl iodide [13,57,200], propyl iodide [13], butyl iodide [44], 4-nitrobenzyl bromide [44], monochloroacetic acid [18,19,37,40, 41,198], and diazomethane [108,109,129] are used as alkylating agents.

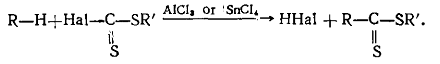
The Friedel–Crafts synthesis of dithiocarboxylic acid esters is used in several versions. The reaction of pyrazolone derivatives with carbon disulphide and ethyl bromide gives rise to the ethyl esters [132,133,207,208]:

$$\mathrm{R{-}H + C_2H_5Br + CS_2 \xrightarrow{AlCl_3} HBr + R{-}CS{-}S{-}C_2H_5}.$$

The esters of aromatic dithiocarboxylic acids containing the OH group in the aromatic moiety can be obtained in two ways [208,209,210]:

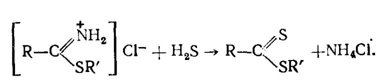


Esters of halogenodithiocarbonic acid may be used in the Friedel–Crafts synthesis instead of carbon disulphide [211,212]:



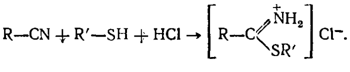
$$\mathrm{R{-}H + Hal{-}\underset{\overset{\|}{S}}{C}{-}SR' \xrightarrow{AlCl_3\ or\ SnCl_4} HHal + R{-}\underset{\overset{\|}{S}}{C}{-}SR'}.$$

Another group of methods for the synthesis of dithiocarboxylic acid esters is based on the interaction of the salts of thioiminoesters with carbon disulphide in an anhydrous medium:



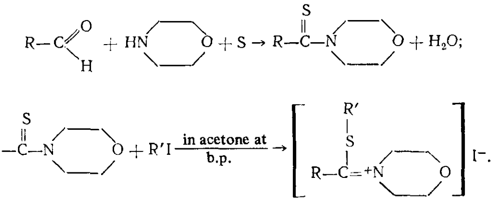
$$\left[\mathrm{R{-}C}\begin{smallmatrix}\mathrm{\overset{+}{N}H_2}\\ \mathrm{SR'}\end{smallmatrix}\right]\mathrm{Cl^-} + \mathrm{H_2S} \rightarrow \mathrm{R{-}C}\begin{smallmatrix}\mathrm{S}\\ \mathrm{SR'}\end{smallmatrix} + \mathrm{NH_4Cl}.$$

Ethyl ester was initially proposed as a solvent for this reaction [130], but higher yields are obtained in dry pyridine [213]. The thioiminoester salts required for the synthesis can be obtained by adding hydrogen chloride to a mixture of equivalent amounts of a nitrile and a thiol [214,215]:



$$\mathrm{R{-}CN + R'{-}SH + HCl} \rightarrow \left[\mathrm{R{-}C}\begin{smallmatrix}\mathrm{\overset{+}{N}H_2}\\ \mathrm{SR'}\end{smallmatrix}\right]\mathrm{Cl^-}.$$

When R = H, i.e. when HCN reacts with thiols, the products are the corresponding dithioformic acid derivatives [216]. The product of the addition of HCN to ketones, i.e. $R_1R_2C(OH)CN$ react with thiols to form thioiminoester salts of the type $\left[\mathrm{R_1R_2C(OH){-}C}\begin{smallmatrix}\mathrm{\overset{+}{N}H_2}\\ \mathrm{SR'}\end{smallmatrix}\right]\mathrm{Cl^-}$ which can also be used [217] to synthesise the corresponding dithiocarboxylic acid esters $R_1R_2C(OH)CSSR'$. Treatment of the latter with thionyl chloride ($SOCl_2$) leads to the substitution of the hydroxy-group by chlorine [217]. It has been suggested recently [218] that thioiminoester salts be obtained from the thioamides $\mathrm{R\overset{\overset{S}{\|}}{C}NH_2}$ and ethyl thiochloroformate ($\mathrm{Cl\overset{\overset{O}{\|}}{C}SC_2H_5}$). Thioiminoester salts in which the hydrogen atoms at the nitrogen atom have been substituted by hydrocarbon groups, i.e. $\left[\mathrm{R{-}C}\begin{smallmatrix}\mathrm{\overset{+}{N}R_3R_4}\\ \mathrm{SR'}\end{smallmatrix}\right]\mathrm{Cl^-}$ can also be used to synthesise dithiocarboxylic acid esters [219,220]. In the specific instance of morpholine, the latter can be represented by the fragment $=\overset{+}{\mathrm{N}}\begin{smallmatrix}\mathrm{R_3}\\ \mathrm{R_4}\end{smallmatrix}$. [54,134,197,221]. Thioiminoester salts can be obtained [221] as follows:

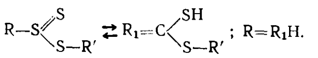


Methods have also been proposed for the synthesis of dithiocarboxylic acid esters by the interaction of unsaturated compounds with thiols [222,223] or with dithiocarboxylic acids [224]. On heating, 2-mercapto-1,1-diphenyl-2-phenylthioethylene is transformed into the phenyl ester of diphenylmethanedithiocarboxylic acid [225]. Methods have also been developed for the synthesis of fluoro-substituted dithiocarboxylic acids [226].

2. Properties of the Esters

The esters RCSSR′, in which both organic groups are aliphatic, are yellow or orange oily liquids. This also applies to cyclohexane- and phenylmethane-dithiocarboxylic acids. However, the esters of dithioformic acid (R = H) are trimeric and therefore crystalline [13,200]. If R is an aromatic group and R′ an aliphatic group, the esters can be both liquid and crystalline red substances. The esters with both groups are aromatic crystalline substances.

If the group R contains substituents capable of splitting off a proton, the ester can exist in two forms, involved in tautomeric equilibrium [171,227,228]:



$$\mathrm{R{-}S}\begin{smallmatrix}\mathrm{S}\\ \mathrm{S{-}R'}\end{smallmatrix} \rightleftarrows \mathrm{R_1{=}C}\begin{smallmatrix}\mathrm{SH}\\ \mathrm{S{-}R'}\end{smallmatrix};\ \mathrm{R{=}R_1H}.$$

Dithiocarboxylic acid esters are insoluble in water, but are usually readily soluble in many organic solvents. When such solutions are heated, thermochromic phenomena may be observed. For example, a solution of methyl naphthalene-1-dithiocarboxylate in ethyl benzoate or ethyl oxalate as well as a solution of phenyl diphenylmethanedithiocarboxylate in xylene change colour on heating. When the solutions are cooled, the initial colour is restored [27,229].

The electronic absorption spectra of the esters differ little from those of the acids themselves [152]. The absorption spectra of the methyl esters of ethane- [205], cyclohexane- [230], benzene- [230], 2,4-dihydroxybenzene- [146], naphthalene-1- [229,230], and naphthalene-2-dithiocarboxylic [230] acids, the ethyl esters of methane- and benzene-dithiocarboxylic acids [152], and the phenyl esters of benzene-, 4-hydroxybenzene-, 2, 4, 6-trimethylbenzene-, and 2-thiophen-dithiocarboxylic [212] acids have been published.

Characteristic absorption maxima at 1050 and 1240 cm^{-1} have been observed in the vibration spectra of the methyl, ethyl, and phenyl esters of aromatic dithiocarboxylic acids[212]. The absorption wavenumbers of the ethyl and isobutyl esters of methanedithiocarboxylic acid as well as the ethyl and butyl esters of ethanedithiocarboxylic acid have been published[213]. The spectra themselves have been published only for the methyl esters of 3-methyl-1-phenyl-5-pyrazolone-4-dithiocarboxylic acid (500–4000 cm^{-1})[199] and 2,4-dihydroxybenzenedithiocarboxylic acid (685 to 3800 cm^{-1})[146].

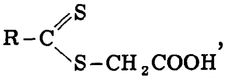
The magnetic permeability of ethyl methanedithiocarboxylate has been determined[231] as well as the NMR chemical shifts of the protons in the ethyl esters of methane-, phenylmethane-, and benzene-dithiocarboxylic acids and methanebis(dithiocarboxylic) acid[232]. The chemical shifts of carbon-13 have also been determined in the last instance[233].

Among the chemical properties of the esters, their ability to hydrolyse to the corresponding dithiocarboxylic acids has already been noted. However, the effect of hydrolysing agents can also lead to monothiocarboxylic or even carboxylic acids[132,203,208,234].

When the methyl esters of aliphatic and aromatic dithiocarboxylic acids are reduced with amalgamated zinc in hydrochloric acid, the main reaction product is the sulphide RCH_2SCH_3, in which the thiono-sulphur atom of the ester has been replaced by two hydrogen atoms[54]. In the polarographic reduction[54] of these esters, the half-wave potentials were in the range between –1 and –1.5 V. The half-wave potentials have also been determined for a number of phenyl esters[212], ranging from –0.95 to –1.30 V.

3. Applications of the Esters

The esters are usually much more stable than the dithiocarboxylic acids themselves. For this reason, they frequently constitute the form in which dithiocarboxylic acids are stored and actually used (for example, for thioacylation[235,236]). The carboxymethyl esters



$R-C(=S)-S-CH_2COOH$

, which form water-soluble alkali metal salts, are particularly convenient for this purpose[37,40,41,237]. When necessary, the dithiocarboxylic acids can be obtained by hydrolysing the esters[130].

The ability of the esters to condense with nitriles, which are CH acids, and to undergo self-condensation can be used also in organic synthesis[238]. The esters can also serve as the starting materials in the synthesis of keten thioacetals[239] or as intermediates in the synthesis of dyes[119,196]. The dyes obtained from the esters of dithiocarboxylic acids of type (XI) proved to be extremely valuable sensitisers in the manufacture of photographic materials[119]. It has been stated in the literature that the esters can be used as antioxidants in lubricating oils[224] and also as bactericidal and fungicidal agents[91].

V. METAL DITHIOCARBOXYLATES

1. Synthesis and Properties

There is an ionic bond between the anion and cation in alkali and alkaline earth metal dithiocarboxylates. For this reason, they are readily soluble in water. Aqueous solutions of the dithiocarboxylates are usually obtained by the reaction of dithiocarboxylic acids with solutions of alkalies. Many sodium and potassium dithiocarboxylates are stable in aqueous solutions for several months[45]. However, alkali metal cyanodithioformates decompose rapidly in aqueous solutions[138] and alkali metal trifluoromethanedithiocarboxylates cannot be obtained at all because of the strong electron-attracting influence of the trifluoromethyl group[137]. Sodium benzenedithiocarboxylate[42,156] and phenylmethanedithiocarboxylate[156] have been obtained in a solid form by the vacuum evaporation of their aqueous solutions, while evaporation of methanol solutions yielded potassium dithioformate[15,240]. Potassium pyridine-4-dithiocarboxylate has been obtained in the solid state by adding ethyl ether to an evaporated methanol solution of the salt[23].

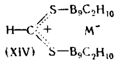
Ammonium dithiocarboxylates are also readily water-soluble ionic compounds. Only ammonium 2-aminocyclopent-1-ene-1-dithiocarboxylate is precipitated from ammonia solutions[84,241]. Quaternary ammonium dithiocarboxylates can be obtained in a crystalline form. In many instances, they are precipitated when aqueous solutions of sodium dithiocarboxylate and the quaternary ammonium halide are mixed. The corresponding salts of naphthalene-1-[49,149,242], naphthalene-2-[50,64], 2-hydroxybenzene-[145], 1-hydroxynaphthalene-2-[243], and indole-3-dithiocarboxylic[53] acids have been obtained in this way. In other instances, cooling or extraction with chloroform followed by the addition of another solvent which causes precipitation are used to isolate the reaction product. Quaternary ammonium salts of thioformic[240] and benzene-, 4-chlorobenzene-, 4-methylbenzene-[244], phenylmethane-[245], quinoline-2-, and quinoline-4-dithiocarboxylic[24] acids have been obtained by this procedure. In the synthesis of tetraethylammonium cyanodithioformate, tetraethylammonium hydroxide is used instead of the corresponding halide[138].

A series of tetraphenylphosphonium[53,148,153,240], tetraphenylarsonium[15,24,139,149,154,240,242], and triphenyltin[240] dithiocarboxylates have also been synthesised. The solubilities of certain 'onium naphthalene-[149], pyrrole- and indole-dithiocarboxylates[246] have been determined.

The introduction of transition or non-transition metal ions into aqueous solutions of ionic dithiocarboxylates often gives the corresponding dithiocarboxylate chelate complexes. The latter are insoluble in water and are precipitated. Among non-transition elements, gallium, indium, thallium, germanium, tin, lead, arsenic, antimony, bismuth, and selenium ions react with dithiocarboxylate ions. Among transition metals, dithiocarboxylate chelates are formed by vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, osmium, rhodium, iridium, palladium, platinum, copper, silver, gold, zinc, cadmium, and mercury ions. The dithiocarboxylates of the majority of platinum metals are formed slowly at the usual temperature, but the reactions can be accelerated by heating. It has been stated in the literature that dithiocarboxylate ions interact with zirconium ions[108]. Among the actinides, uranium interacts with dithiocarboxylate ions.

Metal dithiocarboxylates can also be obtained from organometallic compounds as a result of the dissociation of the C–M bonds and the insertion of carbon disulphide at the site of the break; part of the review of Butler and Fenster[247] is devoted to this problem. Such reactions also include the interaction between organometallic compounds and carbon disulphide, used to synthesise dithiocarboxylic acids (see Section II). It has been stated in the literature that dialkyl-aluminium-, -gallium, and -indium dithiocarboxylates can be obtained in this way[248], although later the same author synthesised these substances by a different method [249]. The method has been used successfully to prepare manganese and rhenium dithiocarboxylatocarbonyls having the general formula $RCSSM(CO)_4$, where R = CH_3, C_6H_5, $CH_3C_6H_4$, ClC_6H_4, $C_6H_5CH_2$, or $(C_6H_5)_3C$.[250-253] However, the attempts to obtain triethyl-lead ethanedithiocarboxylate from tetraethyl-lead and carbon disulphide were unsuccessful[254]. Manganese and rhenium dithiocarboxylatocarbonyls can also be synthesised from the corresponding dithiocarboxylic acids (benzene- [20,255,256] and trifluoromethanedithiocarboxylic acids [135]) or their chlorides (C_6H_5CSCl).[257]

In addition, the following complexes containing dithioformate ions as ligands have been obtained from mixed dithiocarboxylates: $Re(CO)_2(HCSS)[P(C_6H_5)_3]_2$, [258] $[Ru(HCSS)_2][P(C_6H_5)_3]_2$, [259] and compound (XIV).[260-262] Their structures have been elucidated by X-ray diffraction:



(XIV) ; M = Co, Fe .

2. Absorption Spectra

The first electronic absorption spectra of metal dithiocarboxylates were already obtained in the 1920's [152]. However, the bulk of the data on these spectra have been published the last 7–8 years. The spectra or numerical data characterising the absorption maxima of a number of metal dithioformates[15,240], methane- [152,153,163,263], ethane- [153], trimethylmethane- [163], phenylmethane- [155,156,163,263-268], cyclohexane- [154], benzene- [152,156,163,264,269-274], 2-hydroxybenzene- [275], 4-hydroxybenzene- [159,276], 2,4-dihydroxybenzene- [277,278], 2,3,4-trihydroxybenzene- [277], 4-hydroxy-3-methoxybenzene- [147], 4-chlorobenzene- [270,271,274,279], 4-methylbenzene- [163,270-274], napthalene-1- [280], 1-hydroxynaphthalene-2- [243], pyrrole- and indole- [281], and 2-aminocyclopent-1-ene-1-dithiocarboxylates [84] have been described in the literature.

Comparison of the absorption spectrum of the dithioformate ion with that of the thioloformate ion $HCOS^-$ led[240] to the following assignments: 225 nm to the $n - \sigma^*$ transitions, 331 nm to the $\pi-\pi^*$ transitions, and 386 nm to the $n-\pi^*$ transitions.

The electronic absorption spectra of lead, indium, chromium(III), cobalt(III), rhodium(III), iridium(III), nickel(II), palladium(II), and platinum(II) benzene- and phenylmethane-dithiocarboxylates led to the conclusion [156] that the chromophoric groups MS_4 in the ML_2 complexes have the square planar structure, while in the ML_3 complexes the MS_6 chromophores are pseudo-octahedral. A preliminary assignment was also made of the absorption bands (the Figure presents as an example the spectrum of nickel benzenedithiocarboxylate).

The bands in the ranges 208–222 and 250–268 nm were assigned to the vibrations of the benzene ring. One or several intense bands in the range 295–345 nm were assigned to the $n-V$ transitions. The bands which originate from the electronic transitions in the conjugated system of the benzene ring and the dithiocarboxylate group are located between those of the benzene ring and the $n-V$ transitions. In the range 333–455 nm, there are bands which are missing from the spectra of the free ligands. They were assigned to the charge-transfer (CT) bands. In the spectra of the transition metal compounds, there are weak absorption bands above 455 nm due to the $d-d$ transitions in the MS_4 and MS_6 chromophores.

Later, approximately the same assignments were made in the electronic absorption spectra of vanadium [263], nickel, and zinc [163] methanedithiocarboxylates, nickel trimethylmethanedithiocarboxylate [163], iron[264], vanadium[263], nickel, and zinc[163] benzenedithiocarboxylates, vanadium[263], nickel, and zinc [163] 4-methylbenzenedithiocarboxylates, and iron[264], vanadium [263], nickel, and zinc [163] phenylmethanedithiocarboxylates.

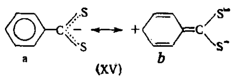
The electronic absorption spectra of arsenic, bismuth, indium, gallium, antimony, mercury(II), lead, tin(II), zinc, and platinum(II) 2,4-dihydroxybenzenedithiocarboxylates led to the conclusion[278] that the absorption band in the range 390–420 nm arises as a result of $n-\pi^*$ transitions. This is nevertheless difficult to accept, since this band is intense (the molar extinction coefficients are between 4×10^4 and 8×10^4).

The vibrational spectra or the wavenumbers in these spectra have been published for a number of metal dithioformates [15,240], cyanodithioformates [166], and methane- [168,252,253,263,282], 2-aminocyclopent-1-ene-1- [84,283], benzene- [252,253,263,284-288], 4-methylbenzene- [253,263,289], 4-chlorobenzene- [253], 4-isopropylbenzene- [289], 2,4-dihydroxybenzene- [290], and naphthalene-1-dithiocarboxylates[285]. The following assignments were made in the spectrum of potassium dithioformate [240] (the wavenumbers are in cm^{-1}): 1250 to $\delta_{asym}(SCS)$, 988 to ν_{asym} (SCS), and 848 to ν_{sym} (SCS).

Comparison of the spectra of sodium and lead methanedithiocarboxylates with those of their deuterated analogues led to the following assignments[282]: 1141 to $\rho(CH_3)$, and $\nu_{asym}(CSS)$, 602 to $\nu_{sym}(CSS)$, 464 to $\omega(CSS)$, 372 to $\delta(CSS)$, and 348 to $\rho(CSS)$. The following assignments were made in the spectra of mixed methanedithiocarboxylatocarbonyl complexes [252,253]: 1146 to $\nu_{asym}(CS_2)$ and 616 to $\nu_{sym}(CS_2)$. Calculation [168] of the normal vibrations of the methanedithiocarboxylate ion and its deuterated analogue permitted the following assignments:

2976 cm^{-1} to CH stretch.;
2915 cm^{-1} to CH stretch.;
1449 cm^{-1} to CH def.;
1349 cm^{-1} to CC stretch. + CH def.;
1141 cm^{-1} to CC stretch. + CS stretch. + SCS def. + CCS def.;
1115
1065 cm^{-1} to CS stretch. + SCC def. + CH def.;
983 cm^{-1} to CH def.;
865 cm^{-1} to CS stretch. + SCC def. + CH def.;
602 cm^{-1} to CS stretch. + CS stretch.;
372 cm^{-1} to SCS def. + SCC def.;
348 cm^{-1} to SCC def.

A number of studies have been made on the spectra of benzenedithiocarboxylates, but the assignments are not unambiguous. In the spectra of lead, cadmium, and thallium benzenedithiocarboxylates, the wavenumbers in the range 940–1000 cm^{-1} are attributed to the vibrations in the CS_2 group[284]. In the study [286,287] of the spectra of nickel(II), palladium(II), cobalt(III), chromium(III), indium, rhodium(III), lead, and iron(III) benzenedithiocarboxylates, comparison with the spectra of the complexes of the deuterated analogues led to the following assignments: 980–1000 to $\nu_{asym}(CSS)$; 940–950 to $\nu_{sym}(CSS)$; 660–670 to $\delta(CSS)$; 360–370 to $\nu_{asym}(MSS)$; and 310–320 to $\nu_{sym}(MSS)$. Furthermore, the differences between the vibrational wavenumbers of the benzene ring in various complex-forming agents led to the conclusion that the contribution of the resonance form of the ligands (XVb) increases with increase of the electron affinity of the central ion:



(XV)

A subsequent study[288] of the spectra of potassium, thallium(I), lead, cadmium, mercury(II), and indium benzenedithiocarboxylate nevertheless provided a justification for a new assignment of certain wavenumbers. The 585–589 cm^{-1} was assigned to the γ(CSS) vibrations and the 320–330 cm^{-1} band to the δ (CSS) vibrations. Objections were raised against the assignment of the 950 cm^{-1} band to the $\nu(CS_2)$ vibrations and of the 670 cm^{-1} band to the δ (CSS) vibrations. The band at 300–350 cm^{-1} was assigned to the latter.

The following assignments were made in the spectra of mixed benzenedithiocarboxylatocarbonyl complexes[252,253]: 1267 to $\nu_{asym}(CS_2)$; 613–631 to $\nu_{sym}(CS_2)$. Assignments were also made in the spectra of 4-methylbenzene-[253,289], 4-chlorobenzene-[253], and 4-isopropylbenzene-dithiocarboxylates[289]. The 1220–1260 cm^{-1} and 590 cm^{-1} bands in the spectra of 2,4-dihydroxybenzenedithiocarboxylates were assigned to the stretching vibrations in the CS_2 group. The bands in the range 970–990 cm^{-1} were assigned to the vibrations of the same group.

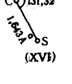
The bands in the range 990–1020 cm^{-1} in the spectra of naphthalene-1-dithiocarboxylates[285] were assigned to the stretching vibrations of the CSS group.

The Structure of Metal Dithiocarboxylates

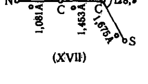
The magnetic properties of iron(III), benzene- and phenylmethane-dithiocarboxylates indicate the presence of low-spin complexes[264,291]. Cobalt(III), indium, rhodium(III), palladium(II), iridium(III), and platinum(II) phenylmethanedithiocarboxylates are diamagnetic, while the corresponding chromium(III) complexes are paramagnetic[156]. Nickel(II), platinum(II), copper(II), zinc, and cadmium 2-aminocyclopent-1-ene-1-dithiocarboxylates are also diamagnetic, which indicates a square planar coordination of the sulphur atoms[283,292]. Magnetic moment measurements have shown[263,293] that vanadium functioning as the complex-forming agent in methane-, phenylmethane-, benzene-, and 4-methylbenzene-dithiocarboxylates is in the +4 state of oxidation. Judging from their magnetic properties[163], nickel methane-, trimethylmethane-, phenylmethane-, benzene-, and 4-methylbenzene-dithiocarboxylates are low-spin complexes. The magnetic permeability of copper(I) naphthalene-1-dithiocarboxylate has also been determined[294].

The number of ESR data is so far small[263,295,296].

A number of metal dithiocarboxylates have been investigated by X-ray diffraction and their structures have been elucidated. The principal data obtained in the study of potassium dithioformate[297] are presented in formula (XVI). In the mixed dithioformatocarbonyl complexes[258,259], the C–S bond length is in the range 1.64–1.70 Å. The data obtained for the cyanodithioformate ion[298,299] are presented in formula (XVII):



(XVI)

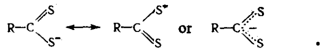


(XVII)

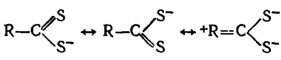
The sulphur atoms around the central atom in zinc benzenedithiocarboxylate $Zn(C_6H_5CSS)_2$ form a strongly distorted tetrahedron[300], while in vanadium benzenedithiocarboxylate $V(C_6H_5CSS)_4$ and phenylmethanedithiocarboxylate $V(C_6H_5CH_2CSS)_4$ they form an almost ideal dodecahedron[263,301,302] and in chromium benzenedithiocarboxylate $Cr(C_6H_5CSS)_3$ a distorted octahedron[303]. Crystalline nickel trimethylmethanedithiocarboxylate $Ni[(CH_3)_3CCSS]_2$ is dimeric, since bonds are formed between the nickel atoms and the sulphur atoms in another molecule[304]. The coordination of the sulphur atoms is square planar. Nickel phenylmethanedithiocarboxylate $Ni(C_6H_5CH_2CSS)_2$ is also dimeric, but in this case there is a bond between the nickel atoms[305]. The sulphur atoms surrounding each nickel atom are located in the same plane. Nickel benzenedithiocarboxylate $Ni(C_6H_5CSS)_2$ is a trimer formed by bonds between the nickel atoms and the sulphur atoms in another molecule[306]. The coordination of sulphur atoms about the nickel is square planar.

In dimeric palladium benzenedithiocarboxylate $Pd(C_6H_5CSS)_2$, there are bonds between the palladium and the sulphur atoms in another complex molecule[307]. However, the platinum 4-isopropylbenzenedithiocarboxylate dimer $Pt(C_3H_7C_6H_4CSS)_2$ is formed as a result of bonds between the platinum atoms[289,308]. The sulphur atoms in this compound form a square antiprism, two faces of which contain platinum atoms. Two ligands are then in the bridging positions and are linked to both platinum atoms.

In all the dithiocarboxylates investigated by X-ray diffraction, the two bonds between carbon and sulphur are virtually identical, which indicates the equalisation of electron density:



The length of the bond between the carbon of the dithiocarboxy-group and the carbon of the group R depends on the nature of the latter. If it is aliphatic (this also applies to $C_6H_5CH_2$), the length of this bond corresponds to that of a single bond. However, if the group is aromatic (C_6H_5), the bond length is in the range 1.5–1.5 Å, which indicates a partial double bond character of the linkage, i.e. conjugation over the entire ligand, which is consistent with the conclusions reached in the study of vibrational spectra [see formula (XV)]. Thus three resonance forms contribute to the structure of the ligand:



4. Complex Metal Dithiocarboxylates in Solution

Complex dithiocarboxylates can be extracted from an aqueous medium by organic solvents. The extractability of metal benzene-[309], naphthalene-1-[310], pyrrole- and indole-[53], and quinoline-2- and quinoline-4-dithiocarboxylates[162] by various extractants has been tested qualitatively. The dependence of the optical density of the extract on the pH of the aqueous phase has been elucidated for the extraction of cyclohexane-[154], phenylmethane-[155,265–268], benzene-[269,274], 2-hydroxybenzene-[148,275], 4-hydroxybenzene-[159,276], 2,4-dihydroxybenzene-[277,278], 2,3,4-trihydroxybenzene-[277], 3,4-methylenedihydroxybenzene-[148], 4-chlorobenzene-[270,271,274,279], 4-methylbenzene-[270-274], naphthalene-1-[280], naphthalene-2-[50], furan-2-[148], indole-, and pyrrole-dithiocarboxylates[281,311]. Many of these are extracted from an extremely acid medium.

The molecular weights of chromium(III), cobalt(III), indium, rhodium(III), palladium(II), iridium(III), and platinum(II) phenylmethane- and benzene-dithiocarboxylates dissolved in benzene have been determined by the osmometric method[156], which has also been used to determine the molecular weights of iron(III) phenylmethane- and benzene-dithiocarboxylates in chloroform solutions[264]. The molecular weights of vanadium methane-, phenylmethane, benzene-, and 4-methylbenzene-dithiocarboxylates[263], nickel methane-, trimethylmethane-, phenylmethane-, and benzene-dithiocarboxylates[163], and of the mixed complex[20] $C_6H_5CSSMn(CO)_4$ in solutions have also been determined. Polymeric species were not detected, with the exception of nickel trimethylmethanedithiocarboxylate.

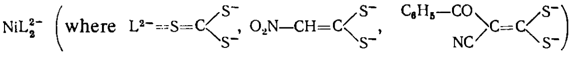
The usual methods have been employed to determine the compositions of the dithiocarboxylates extracted: the isomolar series [continuous variations], molar ratios, equilibrium shift, and other methods as well as the dependence of the formation function[312] and the Leden function[313] on the excess of ligands. In most cases, the composition of the complexes is consistent with the valence of the complex-forming agent[147,159,267-271,273-275,277,278,280,287,311]. However, there are exceptions. For example, nickel forms several compounds[159,276], bivalent cobalt reacts in proportions of 1 : 3, [159,267,270,275,277,287], and molybdenum(V, VI) reacts in proportions of 1 : 2 or 1 : 3. [147,275,277,280]

The stability constant of osmium 2-aminocyclopent-1-ene-1-dithiocarboxylate (2.5×10^9) has been determined in aqueous ethanol[314]. The two-phase stability constants of a number of dithiocarboxylates (the ratios of the concentrations of the complexes in the organic phase to the products of the concentrations of metal ions and free ligands in the aqueous phase) have been determined for a number of dithiocarboxylates. The constants for naphthalene-1-dithiocarboxylates in the water–chloroform system[315] are between 10^9 and 10^{40}. The two-phase stability constants of hydroxybenzenedithiocarboxylates found in the water–3-methylbutanol system[316] are in the range from 10^9 to 10^{22} and those of 2,4-dihydroxybenzenedithiocarboxylates[278] are in the range between 10^5 and 10^{16}.

Attempts have been made at a chromatographic separation of naphthalene-1-dithiocarboxylates using toluene–heptane mixtures as the solvent[317,318].

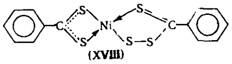
5. Metal Perthiocarboxylates

At the end of the 1940's, it was observed[319] that nickel benzenedithiocarboxylate $(C_6H_5CSS)_2Ni$ combines with sulphur to form a compound in which there are 5 sulphur atoms for each nickel atom. Immediately after the establishment of this fact, it was suggested that the compound formed is a dinuclear complex of nickel(IV). [319-321]. However, the study of the reactions involving the addition of elemental sulphur to ene-1,1-dithiol complexes of nickel



$$NiL_2^{2-}\ \left(\text{where } L^{2-}{=}S{=}C(S^-)_2,\ O_2N{-}CH{=}C(S^-)_2,\ (C_6H_5{-}CO)(NC)C{=}C(S^-)_2\right)$$

showed that the nickel remains bivalent under these conditions and the sulphur atom is inserted in the four-membered chelate ring, expanding it into a five-membered ring[322]. This suggested that sulphur adds similarly to nickel benzenedithiocarboxylate. Somewhat later, it was shown[323] that this does indeed entail the formation of nickel benzeneperthiocarboxylate benzenedithiocarboxylate(XVIII):



(XVIII)

A number of other perthiocarboxylate dithiocarboxylates as well as perthiocarboxylates of metals such as zinc, nickel, iron(III), cobalt(III), palladium(II), and platinum(II) have also been obtained[292,324-327]. For this purpose, zinc perthiocarboxylates are synthesised first. The corresponding aldehyde RCHO in tetrahydrofuran solution is treated with $(NH_4)_2S_2$ and the resulting perthiocarboxylate ions are precipitated in the form of the nickel complex $(RCSSS)_2Zn$. The latter complex is used to synthesise the perthio-complexes of other elements with the aid of the corresponding double decomposition reactions.

Nevertheless, one should note that the formation of perthio-complexes has also been observed in the direct interaction of bivalent nickel and cobalt ions with 2-aminocyclopent-1-ene-1-dithiocarboxylate ions; one molecule of the reactant then decomposes and liberates a sulphur atom, which is necessary for the formation of the five-membered chelate ring[292].

The electronic absorption spectra of a number of perthio- and perthio-dithio-complexes have been published[163,324,326]. On passing from nickel benzenedithiocarboxylate to the benzeneperthiocarboxylate benzenedithiocarboxylate, the charge-transfer band undergoes a hypsochromic shift (approximately 60 nm) and, on passing to the nickel bis(perthio)-complex, the shift is even greater (approximately 180 nm). [324]

X-Ray diffraction analysis of zinc[328], nickel[326-328], and iron(III)[325,329], perthiocarboxylate complexes has shown that all the atoms of the five-membered chelate ring are in the same plane.

6. Applications of Metal Dithiocarboxylates

In view of their high stability in air and in aqueous alkaline solutions, quaternary ammonium, phosphonium, and arsonium dithiocarboxylates can be used as a convenient form for the storage of dithiocarboxylic acids. These compounds have also been proposed as analytical reagents[242].

Dithiocarboxylates are used in analytical chemistry to detect and determine the corresponding elements. Sodium antipyrine-, 3-antipyrine-, and isoantipyrine-dithiocarboxylates have been proposed for the detection of nickel ions[330]. Tervalent arsenic can be detected with the aid of tetraethylammonium naphthalene-1-dithiocarboxylate[331].

Palladium cyclohexanedithiocarboxylate can be used for the extraction-photometric determination of this element[154]. Palladium benzenedithiocarboxylate[332], iron 4-methyl- and 4-chloro-benzenedithiocarboxylates[165], molybdenum 4-hydroxy-3-methoxy-benzenedithiocarboxylate[147], nickel 4-hydroxy-benzenedithiocarboxylate[276], arsenic naphthalene-1-dithiocarboxylate[333], nickel 2-hydroxynaphthalenedithiocarboxylate[334], and nickel 2-aminocyclopent-1-ene-1-dithiocarboxylate[241] have been suggested for the extraction-photometric determination of the corresponding elements. In the case of nickel 1-hydroxynaphthalenedithiocarboxylate[335] and osmium 2-aminocyclopent-1-ene-1-dithiocarboxylate[314], photometric measurements are made on ethanol solutions in which the solubility of these complexes is fairly high. Nickel 2-hydroxynaphthalenedithiocarboxylate can also be used for the gravimetric determination of nickel[334].

Several methods for the quantitative determination of the elements with the aid of antipyrine-, 3-antipyrine-, and isoantipyrine-dithiocarboxylic acids have been proposed. Nickel[330] and cobalt[336] can be determined gravimetrically with the aid of these reagents. A solution of cobalt antipyrine-4-dithiocarboxylate in pyridine is suitable for the photometric determination of cobalt[337]. A chloroform solution of nickel antipyrine-4-dithiocarboxylate can be used for the determination of mercury: the decrease of colour intensity on shaking with solutions of mercury salts is proportional to the amount of mercury[338]. The double decomposition reaction occurring when an aqueous solution of nickel nitrate is shaken with chloroform solutions of bismuth, lead, and thallium antipyrine-4-dithiocarboxylates can be used for the photometric determination of the last three elements[339].

Many metal dithiocarboxylates are highly effective fungicides and can be used to protect fruit trees from fungal disease. Nitromethane-[87,340], benzene-[341], chlorobenzene- (from mono- to penta-chlorobenzene-)[342,343], and 2-hydroxynaphthalene-dithiocarboxylates[341] have been proposed for this purpose. Metal dithiocarboxylates can be used as accelerators of the vulcanisation of raw rubber. It is postulated that they promote the cleavage of the eight-membered sulphur molecule in this process[344].

Various impurity elements can be removed from the surface of silicon $p-n$ structures in the form of 2,4-dihydroxybenzenedithiocarboxylates, which greatly increases the breakdown potential and reduces the leakage current[345]. Water-soluble salts can be freed from heavy metal impurities by adding an ethanol solution of 2,4-dihydroxybenzenedithiocarboxylic acid: the dithiocarboxylates of the impurity elements pass to the solid phase together with the precipitated acid[346].

Tetraethylammonium napthalene-1-dithiocarboxylate, which is an effective flotation agent for many sulphide minerals, has been proposed as the collector in the flotation of ores[347].

VI. QUANTUM-MECHANICAL CALCULATIONS

The energy of the $\pi-\pi^*$ transition in the dithiocarboxylate group has been calculated by the Hückel method[348]. The result obtained agrees well with the experimental absorption of sodium methanedithiocarboxylate.

The energies of the lowest vacant and the highest occupied molecular orbitals have been calculated for nine dithiocarboxylic acids[349]. The energies of the lowest vacant levels are correlated with the polarographic half-wave potentials of dithiocarboxylic acids and their esters[350]. The results of the calculation of the energies of the $n-\pi^*$ and $\pi-\pi^*$ transitions in the molecules of 19 dithiocarboxylic acids agree satisfactorily with the experimental data obtained from the electronic absorption spectra of the corresponding methyl esters[230].

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The Chemistry of Tetranitromethane

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Information on the methods of preparation, physical and chemical properties, and toxicity of tetranitromethane that appeared in print up to 1974 is reviewed systematically. Considerable attention is paid to the diverse reactivity of tetranitromethane with unsaturated compounds that has been discovered during recent years. A list of 317 references is included.

CONTENTS

I. INTRODUCTION

Several research workers have paid close attention to tetranitromethane during the past fifteen years. Thus, whereas around 100 publications appeared during the century after its discovery (Shishkov, 1857), this number had been doubled by 1973. Such vigorous progress in the chemistry of nitromethane is due to the discovery of fundamentally new types of chemical reactions leading to the synthesis of various nitro- and polynitro-compounds. The need therefore arose to summarise the accumulated experimental results, especially as reviews on the chemistry of tetranitromethane are lacking both in the Soviet and in the foreign literature.

Tetranitromethane is a unique nitro-compound, in which a regular tetrahedral structure, absence of polarity, and hence equivalence of all the nitro-groups are combined with great mobility of one of the nitro-groups in chemical reactions, resulting in formation of a nitryl cation NO_2^+ and the dually reactive conjugate trinitromethanide anion $(NO_2)_3C^-$ or the corresponding radical-anions or radical pairs depending on the conditions. Perhaps the most characteristic feature of tetranitromethane—a strong π-acid—is its ability to form with π- or p-electron systems (substituted aryls, alkenes, arylalkenes, dienes, vinyl ethers and esters, etc.) donor-acceptor or charge-transfer complexes which, depending on the structure of the donor and the reaction conditions, are converted into nitroaryls, arylnitroalkenes, α-nitro-ketones, tetranitroalkanes, or dinitroisoxazolidines. The diversity of these transformations constitutes the synthetic value of tetranitromethane.

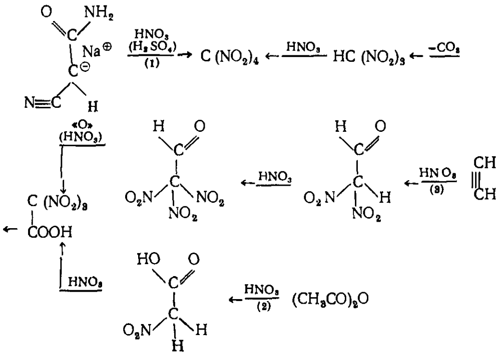
By varying the structure of the donor and the conditions of the reaction we can change the mechanism from heterolytic to radical or radical-ion in photochemical processes, thus changing the direction of the reaction and the structure of the final products, and accomplishing controlled syntheses by means of tetranitromethane.

II. METHODS OF PREPARATION OF TETRANITROMETHANE

Tetranitromethane was first obtained by Shishkov[1,2] in 1857 by the action of a mixture of nitric and sulphuric acids on sodium 2-cyanoacetamide (1), converted further into trinitroacetonitrile, which was then hydrolysed to ammonium trinitromethanide, this being subsequently nitrated with fuming nitric acid to give tetranitromethane. This was the sole method until 1903, when a 10% yield of tetranitromethane was obtained from acetic anhydride and diacetylorthonitric acid[3]. During subsequent years acetic anhydride, acetylene, ethylene, and products of the pyrolysis of natural gas were used as starting materials. Acetic anhydride was nitrated with acetyl nitrate[4], nitrogen pentoxide alone[5] and mixed with nitrogen peroxide[6], and with nitric acid alone[7] and in the presence of glacial acetic acid[8-10] and catalysts (orthophosphoric, sulphuric, and hydrochloric acids, phosphorus pentoxide, phosphoryl chloride, phosphorus pentachloride, sulphuryl chloride, acetyl chloride, and boron triacetate[11]).

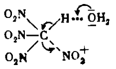
A semi-industrial, convenient, and safe laboratory process giving yields up to 65% was accomplished by nitrating acetic anhydride with nitric acid[12,13]. Nitration takes place in several stages: the nitroacetic acid formed is further nitrated to trinitroacetic acid, which is decarboxylated to trinitromethane, and this is nitrated to tetranitromethane (2).

The use of acetylene and ethylene (Orton, 1918)[14,15] broadened considerably the raw-materials base for the production of tetranitromethane. The nitration of acetylene with 90–97% nitric acid in the presence of oleum or phosphorus pentoxide and mercury nitrate as catalyst also involves trinitroacetic acid and trinitromethane as intermediate species[16] (13).



In 1949 a semi-industrial plant was described for the production of tetranitromethane by the nitration of acetylene[17]. Small industrial plants have been described also for continuous production from pure acetylene[18] and from natural gas by preliminary pyrolysis in an electric arc followed by nitration with a mixture of nitric and sulphuric acids[19].

A study of the kinetics[20] and the mechanism[21] of the final stage in most methods of preparation—the nitration of trinitromethane by nitric acid—showed that, in the presence of 87.5–100% sulphuric acid, the reaction is represented by a third-order equation (containing the concentrations of the nitryl ion, trinitromethane, and water or sulphuric acid) and results from a concerted attack by the nitryl ion at the carbon atom and by the base at the hydrogen atom



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The formation of a small quantity of tetranitromethane (up to 1%) in the manufacture of trinitrotoluene stimulated a search for methods of obtaining the former from aromatic hydrocarbons and their derivatives[22–26]. However, such methods have not found application because of poor yields.

Treatment of keten with 100% nitric acid gives a 90% yield of tetranitromethane[27]. A low yield can be obtained by nitrating acetone with nitric acid[5,28]. The production of tetra- and tri-nitromethanes from malonamide has been patented[29]; a 58% yield of the latter is formed when this diamide is nitrated with 90% nitric acid in the presence of concentrated sulphuric acid, and a 45% yield of the former in the presence of oleum. The interaction of picrylpyridinium nitrate and nitromethane gives a nearly theoretical yield of tetranitromethane[30]. Rather theoretical interest attaches to the Hantzsch method[31], consisting in the reaction of iodotrinitromethane with silver nitrite in aqueous–alcoholic solution, and the analogous action of nitryl chloride on trinitromethane or its silver and potassium salts (yields 65%, 20%, and 94% respectively)[32].

Among the many processes only the nitration of acetic anhydride and that of acetylene have found industrial application. However, the first of these methods has the disadvantage of using large quantities of strong acids, which corrode the equipment, and the second involves the formation of large quantities of gases. The economics of these methods depends on the degree of utilisation and recovery of byproducts.

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

Physicochemical constants determined for tetranitromethane by different workers differ significantly[33], so that it is difficult to use them to describe the structure of the compound or to assess its purity. The values given below have been adopted by the International Bureau of Physicochemical Standards.

Tetranitromethane is a highly volatile, mobile liquid boiling at 127.5°C under normal pressure[34] and melting at 13.9°C.[35] Experimental values of the vapour density have been given[34,36–39] over the range 0–127.5°C, and it can be calculated by means of the equation $\lg p = 7.23 - 2130/T$.[37] The vapour pressure of tetranitromethane has been determined close to its melting point[40]. The density d is respectively 1.64837, 1.63944, and 1.62178 g cm^{-3} at 15, 20, and 30°C. The change in density per degree is 0.00174 g cm^{-3}, and the coefficient of expansion is 0.00109.

The refractive index[41] at 15°C is given by

$$He_r = 1{,}43655,\ dn/dt = 0.00045;\quad H_\alpha = 1{.}43709,\quad dn/dt = 0{,}00045;\quad D_{Na} = 1{.}44066;\quad He_J = 1{.}44076,\ dn/dt = 0.00046;\ He_V = 1{.}44768;\ dn/dt = 0.00046;\quad H_\beta = 1{.}44937,\quad Veviol = 1{.}45593.$$

The dispersion $H\beta - H\alpha = 0.01228$. Molecular refractions[41] are listed in Table 1. The refraction for the nitro-group in tetranitromethane is 7.20 [42] ($MR_D = 31.40$) and 7.248.[43]

Table 1.

	H_α	D	H_β	H_γ
Found	31.16	31.39	31.65	—
Calculated	29.01	29.30	29.72	30.07
Difference	+2.15	+2.09	+1.93	—

Viscosity has been determined experimentally at 15, 20, 30, and 40°C,[35,41,44] and surface tension at 15, 20, 25, 30, and 50°C.[41,54] The parachor of tetranitromethane has also been calculated[45]. The speed of sound in the liquid is 1039 m s^{-1} at 20°C, with a temperature coefficient in the range 4–6 m s^{-1}.[46]

Both the pure compound[47] and its solution in liquid sulphur dioxide[48] showed negligible electrical conductivity. On the other hand, a solution of tetranitromethane in liquid ammonia was very highly conducting[49], probably because of interaction with the solvent. The dielectric constant of tetranitromethane at 5, 20, and 25°C is respectively 2.15, 2.317, and 2.521 s^2 cm^{-2}.[42,47–54] Birefringence has been reported in an electric field, with a molar Kerr constant of 2.98×10^{-12} cm V^{-2}.[55] Experimental dipole moments[52,55–58] lie in the range $(0.19–0.71) \times 10^{-18}$ D at 25°C. Actually, however, the dipole moment of tetranitromethane is zero[6]: the observed values lie within the limits of experimental error, and have been determined on impure samples. One cause of the high value was determination of the dipole moment in solvents (e.g. benzene) capable of forming donor–acceptor complexes with tetranitromethane.

The magnetic susceptibility and the magnetic permeability have been investigated[59–61]. The magnetic refraction and the Cotton–Moulton effect have been examined[62]. Several nuclear magnetic resonance studies have been made[63–69].

The ultraviolet spectrum of tetranitromethane was first obtained by Zelinskii[70], and was later analysed[38,71–75]. The main absorption band in dichloromethane has $\lambda = 280$ nm and $\epsilon = 135$. Discussion of the infrared spectrum[73,76–84] led to the assignments—asymmetric and symmetric stretching vibrations of nitro-groups at 1618 and 1266 cm^{-1} respectively (both very strong); and other bands at 1645 (medium), 1439 (weak), 1370 (m), 990 (w), and 973 (m) cm^{-1} [73]—and interesting studies were made[78,85] of the infrared spectra of the vapour at 25°C, the liquid at 18°C, and the crystalline state at −40, −88, −104, and −126°C. Tetranitromethane can exist in two crystalline forms, with an isomorphous transition at −99.8°C. The Raman spectra obtained in three different states—solid, liquid, and dissolved in tetrachloromethane—indicate that the molecule possesses the symmetry $D_2 = S_{4u} = V_d = 42m$.[86] The main lattice parameters have been determined by means of X-rays[87-93] (see Fig. 1). The diffraction of X-rays has been studied in the liquid and in its solutions[94-96].

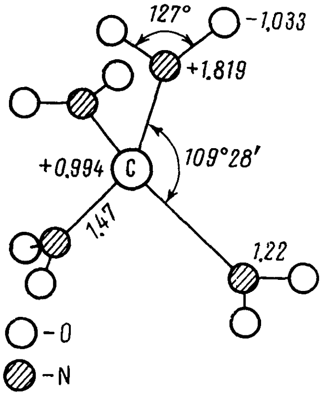


Figure 1. Model of the tetranitromethane molecule.

Heats of formation and combustion were determined[8]:

$$C(\text{diamond}) + 2N_2(\text{gas}) + 4O_2(\text{gas}) = C(NO_2)_4 + 4.7 \text{ kcal mole}^{-1}$$
$$C(NO_2)_4 = CO_2 + 3O_2 + 2N_2 + 89.6 \text{ kcal mole}^{-1}.$$

More recent papers have given more accurate values for the heat of formation (8.9 [97] and 8.8 ± 0.7 [98] kcal mole^{-1}) and the heat of combustion (102.9 kcal mole^{-1} [97,99,100]). Determinations have been made of the latent heat of evaporation[37], the entropy of evaporation[38], and the entropy of vaporisation[101,102]. The energy of dissociation of the carbon–nitrogen bond in tetranitromethane has been estimated as 38.2 [103,104] and 39.3 [105] kcal mole^{-1}. The enthalpy of formation of the compound is 18.5 kcal mole^{-1}.[105,106]

Tetranitromethane is highly toxic[107-112], attacking the respiratory tracts and the central nervous system[112-116]. The threshold concentration is 0.003 mg litre^{-1}, and the permissible limit in air 0.001 mg litre^{-1}.[113-117] Various methods have been worked out for its determination—spectrophotometrically in air and in solutions[113,118,119], calorimetrically in water[120], volumetrically in concentrated nitric acid[121], oscillopolarographically in nitromethane[122], and polarographically in the presence of *m*-dinitrobenzene and 1,3,5-trinitrobenzene[123]—and its use for analytical purposes has been reported[124,125]. Tetranitromethane possesses fungicidal[126,127] and insecticidal[128] properties; data have been published on its biochemical activity[128-131].

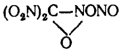
Because of the great mobility of one nitro-group in chemical reactions, many investigators suggested that the four nitro-groups were not equivalent. As a consequence, a structure was in various cases attributed to the compound that explained only the particular reaction, without taking into account the great diversity of its chemical and physicochemical properties.

$C(NO_2)_4$

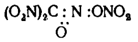
(I)

$(O_2N)_3C—O—NO$

(II)

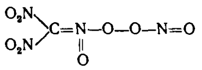


(III)



$(O_2N)_2C : \underset{\ddot{O}}{N} :ONO_2$

(IV)



(V)

In a study of the aci-form of the nitro-group Hantsch[132] suggested the equivalence of all four true nitro-groups (I). Investigation of the behaviour of the compound as a nitrating agent led Schmidt[133] to the nitrite structure (II), adopted by Macbeth[134] on the basis of the similarity in appearance of the ultraviolet spectra of mixtures of tetranitromethane and unsaturated hydrocarbons to those of complexes of alkyl nitrites and unsaturated compounds. Willstätter[135] had deduced the existence of the "cyclic form" (III). Claisen[136] and subsequently Auwers[137] suggested a "nitrone" type of structure (IV) from a study of the physical properties. Finally, examination of the oxidising properties of the compound enabled the "peroxide" structure (V) to be attributed to it[138]. Several investigators assumed[71,139,140] that an equilibrium was established between undissociated and ionic forms.

Later determinations of the dipole moment[56,57,141] and the parachor[45], as well as study of X-ray diffraction patterns[87,94], and the Raman and infrared spectra in the gaseous state[85,142-144] have shown that the molecule has the form of a regular tetrahedron with S_{4u} symmetry.

Quantum-chemical calculation based on the Slater treatment shows[145] that the electron density is considerably raised on the oxygen atoms of the nitro-groups, but significantly lowered on the nitrogen and carbon atoms (Fig. 1).

IV. DONOR–ACCEPTOR (CHARGE-TRANSFER) COMPLEXES

Tetranitromethane is a strong acceptor of electrons and, like Lewis acids, a powerful complexing agent. Its electron affinity has been estimated as 1.7 eV (similar to the value of 1.8 eV for iodine), which is responsible for its great tendency to form complexes with donors[146]. Indeed, one of the most interesting reactions of the compound with alkenes, dienes, arylalkenes, and aryls, yielding a wide range of organic compounds, begins with the formation of charge-transfer complexes, as will be shown below.

The ability of tetranitromethane to form coloured complexes was discovered almost simultaneously by Ostromyslensky[147,148] and by Werner[149] as early as 1909. It is evident as an instantaneous yellow to dark red coloration on addition to a solution of an unsaturated compound. This qualitative test, termed the Ostromyslenskii reaction, is widely used to distinguish tautomeric forms of organic compounds[147,148,150,151] and to detect ethylenic hydrocarbons[152,153], dienes[154], terpenes[155,156], steroids[157], unsaturated ketones[158], dimethylcyclohexanedione derivatives of aldehydes[159], fats and higher unsaturated aliphatic acids[160,161], and aromatic hydrocarbons[150,162-164]. At the same time, this colour reaction is not universally applicable: thus no coloration is observed with benzoic, maleic, and fumaric acids[151], αβ-unsaturated aliphatic acids and their derivatives, αβ-unsaturated aldehydes[154], and halogenated unsaturated compounds[165], owing to the inability of tetranitromethane to form complexes with compounds containing electrophilic groups at the multiple bond. On the other hand, coloured complexes are formed with compounds containing no multiple bond, e.g. cyclopropane[166,167], diethyl sulphide, iodoethane, triethylphosphine, 1,4-dioxan, 1,4-dithian[168-170], dimethyl sulphoxide[171], and various amines[133,172,173]. Not long ago it was proposed that tetranitromethane should be used in the development of chromatograms as a qualitative reagent for organic compounds of bivalent sulphur[174].

Study of the relation between the structure of the unsaturated compound and the colour produced by mixing with tetranitromethane indicated that the intensity of the coloration increased with the basicity of the unsaturated compound[140,175-177]. The ultraviolet spectra of mixtures of aromatic hydrocarbons showed that the colour intensity varied linearly with the concentration of the hydrocarbon and with the number of methyl groups in the benzene ring[178,179].

The mechanism of formation and the structure of the complexes with unsaturated compounds have been discussed since the time of their discovery. Hypotheses involved isomerisation of one or more true nitro-groups into nitrite groups, which form the coloured complex with the alkene[134]. It was assumed also that the coloured complexes were polarised particles retained by electrostatic forces[179,180], or ion-pairs comprising a carbonium ion and a trinitromethanide anion[140,181-183].

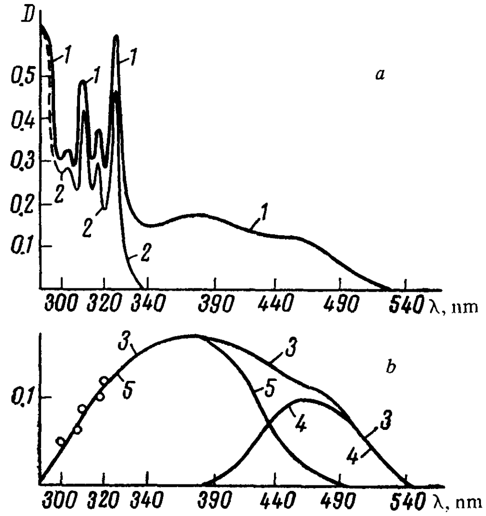


Figure 2. (*a*) Electronic absorption spectrum of 0.80 M tetranitromethane + 0.05 M 2,6-dimethylnaphthalene in heptane: 1) spectrum of tetranitromethane in heptane; 2) long-wavelength region of spectrum of dimethylnaphthalene in heptane. (*b*): 3) spectrum of charge-transfer complex; 4) long-wavelength absorption band of charge-transfer complex; 5) short-wavelength band of charge-transfer complex.

Perekalin et al.[184-189] used electron spectroscopy to study the spectra of the ternary systems formed with a donor and a solvent, in which they detected new bands absent from the initial components, which they ascribed to absorption by the complex. Detailed examination of the charge-transfer spectra with donors, e.g. 2,6-dimethylnaphthalene (Fig. 2), revealed two bands, which were assigned to the same complex[189]. The substantial solvatochroism of the bands due to the complexes, together with their bathochromic displacement with decrease in the ionisation potential of the donor (Table 2), indicated that those at longer wavelengths were intermolecular charge-transfer bands. A modified method of isomolar series throughout the band envelope indicated that the composition of all the charge-transfer complexes was equimolecular[189].

Table 2. Positions of absorption band maxima for charge-transfer complexes in heptane and in nitromethane ν_h and ν_n, extinction coefficients ϵ_{max}, and ionisation potentials *I*.

Donor	ν_h, cm^{-1}	ν_n, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	*I*, eV
Anethole	20 400	21 900	720	—
Hexamethylbenzene	20 600	21 850	1 200	7.8
Tetraphenylethylene	20 750	22 950	4 000	—
Mesitylene	25 800	27 350	3 000	8.4
α-Methylstyrene	25 800	28 050	1 100	—
Benzene	31 300	33 000	10 000	9.2

Table 3. Association constants, products $K_c\epsilon_{max}$, and thermodynamic functions of tetranitromethane complexes in heptane.

Donor	K_c	$K_c\epsilon_{max}$	$-\Delta H_c$, kcal mole^{-1}	$+\Delta G_c$, kcal mole^{-1}	$-\Delta S_c$, cal mole^{-1} deg^{-1}
1,1-Di-*p*-methoxyphenylethylene	0.170	93	1.2	1.0	7.5
Anethole	0.114	81	0.9	1.3	7.5
α-Methylstyrene	0.080	88	0.8	1.5	7.8
β-Methylstyrene	0.045	68	0.7	1.9	8.9
Tetraphenylethylene	0.015	60	0.6	2.5	10.6
Hexamethylbenzene	0.153	180	1.5	1.1	8.8
Mesitylene	0.060	180	1.2	1.6	9.7
Benzene	0.020	190	0.9	2.3	11.0

Thermodynamic parameters calculated for several charge-transfer complexes (Table 3) from a spectrophotometric study of the effect of temperature on the association constants[189,190] reveal the weakness of the complexes ($\nu_c \ll 1$, $\Delta H_c \simeq 1.0$ kcal mole^{-1}, $\Delta G_c > 0$). A definite parallelism is evident between the equilibrium constant and the heats of complex formation, with increase in K_c corresponding to increase in the enthalpy[184,190]. The comparatively slight differences in entropy are evidently due to significant polarisation of the charges accompanying formation of the charge-transfer complexes. The closeness of the product $K_c\epsilon_{max}$ (Table 3) to values characteristic of the homologous series of alkenes ($K\epsilon_{max} \simeq 80$),[184] not to those for alkylbenzenes (~180),[187] shows that π-electrons of the multiple bond, not those of the benzene ring, form the centre of coordination in the charge-transfer complexes of arylalkenes.

The complexes become significantly less stable with increase in the dielectric constant of the medium (Table 4). A clear parallelism is evident between *K* and $(\epsilon - 1)/(\epsilon + 2)$.[189] Determination of the dipole moments of the charge-transfer complexes with various hydrocarbons, by the method of spectral shifts (Table 5), was extremely important in establishing the structure of the complexes. From the dipole moments at 20°C and the spectroscopic characteristics a quasi-ionic structure with separated charges (Fig. 3) was attributed to the charge-transfer complexes in the ground state.

Table 4. Association constants of tetranitromethane complexes of anethole and of isodurene in various solvents at 20 ± 0.1°C.

Solvent	(ε−1)/(ε+2)	Anethole	Isodurene
Heptane	0.234	0.114	0.122
Tetrachloromethane	0.292	0.092	0.065
Diethyl ether	0.530	0.018	0.030
Chloroform	0.560	0.012	0.020
Dichloromethane	0.720	0.006	0.008

Table 5. Calculated individual constants C_I^a and dipole moments of complexes.

Donor	α-Methylstyrene	β-Methylstyrene	Anethole	Benzene	Naphthalene
C_I^a av	2700	2500	1700	2000	3000
μ_g, D	6.0	6.0	5.0	5.0	6.5

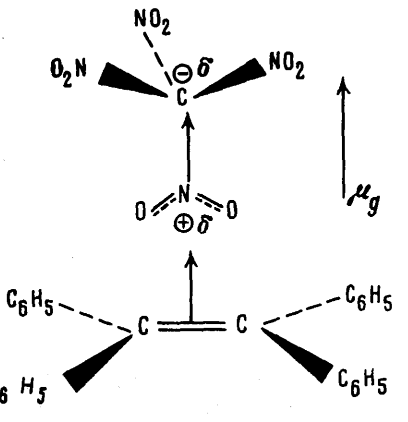


Figure 3. Model of complex of tetranitromethane with tetraphenylethylene.

Existing information on the properties and the structure of the complexes enables us to represent the interaction of unsaturated compounds with tetranitromethane by the scheme

$$\underset{\text{(VI)}}{D + C(NO_2) \rightleftarrows D^{+\delta} \ldots\ldots {}^{-\delta}C(NO_2)_4} \xrightleftharpoons{300\,°K} \underset{\text{(VII)}}{[D \ldots NO_2]^{+\delta}} \ldots {}^{-\delta}C(NO_2)_3$$

$$\rightarrow \text{Transition state} \rightarrow \text{Reaction products}$$

Mixing an alkene with the nitro-compound produces initially charge-transfer complexes of type (VI), which are converted by further interaction of donor and acceptor into charge-transfer complexes with separation of charges (type VII). Redistribution of electron density and change in the steric configuration then convert the latter complexes into a reactive transition state, subsequently settling into the final products depending on its structure and the reaction conditions.

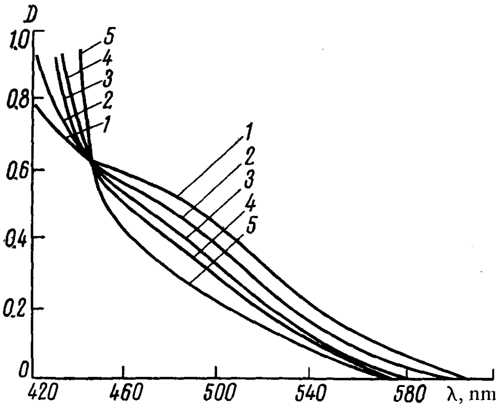


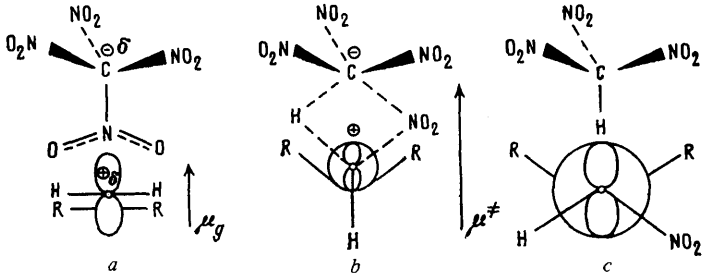
Figure 4. Dependence of electronic absorption spectra on time elapsed from start of reaction (min): 1) 3; 2) 6; 3) 20; 4) 60; 5) 120.

Table 6. Thermodynamic activation parameters for the reaction between tetranitromethane and 1,1-di-*p*-methoxyphenylethylene and electrical characteristics of the transition state.

Solvent	$\frac{\varepsilon-1}{\varepsilon+2}$	$-\ln K_2$		$\Delta H^{\neq}$, kcal mole⁻¹	$-T\Delta S^{\neq}$, kcal mole⁻¹	$\Delta F^{\neq}$, kcal mole⁻¹	ln *A*	$\mu^{\neq}$, D	*Q*
		20° C	30° C						
Heptane	0.235	6.58	5.35	21.4	0.5	20.9	31.3	12	0.60
Tetrachloromethane	0.292	8.09	7.50	9.5	12.2	21.7	9.3	11	0.55
Tetrachloroethylene	0.302	7.62	6.84	5.8	15.6	21.4	3.4	11	0.55
Tetrachloroethane	0.702	6.19	5.57	10.0	10.6	20.6	12.0	12	0.60
Dichloroethane	0.757	5.53	6.41	13.9	6.4	20.3	16.7	12	0.60
Nitromethane	0.926	0.27	1.07	20.8	3.8	17.0	37.0	15	0.80

This process was studied experimentally on the reaction with 1,1-di-*p*-methoxyphenylethylene leading to the formation of 1,1-di-*p*-methoxyphenyl-2-nitroethylene (95%). The presence of a sharp isobiestic point in the electronic spectra in different solvents (Fig. 4) confirmed the hypothetical intermediate formation of a charge-transfer complex. Treatment of experimental kinetic results yielded[189] thermodynamic parameters of the limiting stage and dipole moments of the transition state in various solvents (Table 6). The variation from 0.55 to 0.8 in the degree of charge transfer *Q*, defined as the ratio of the dipole moment μ of the transition state to the maximum value $\mu^{\neq}$ for the ion-pair (~20 D), shows that the transition state occupies an intermediate position between the charge-transfer complex and the ion-pair, approaching the latter.

Conversion of the charge-transfer complex via the transition state into the reaction product (the nitroalkene) is shown diagrammatically in Fig. 5. In the complex the π-electron cloud of the double bond of the donor fits into the electron gap of one of the nitro-groups (Fig. 5*a*), which entails weakening of one of the carbon–nitrogen bonds and strengthening of interaction between the cationoid nitro-group and a carbon atom of the multiple bond. The tendency to $sp^2 \rightarrow sp^3$ rehybridisation of the carbon atoms forming the double bond creates favourable steric conditions (rotation about the carbon–carbon bond) for the quasi-carbonium cation (Fig. 5*b*) to settle into the nitroalkene (Fig. 5*c*). Because of the eclipsed configuration and further weakening of the π-bond, state (*b*) has the highest energy content and hence is the decisive transition state. The stage of detachment of a proton is not rate-determining, as is indicated by the absence of a kinetic isotope effect.



R = *p*-$CH_3OC_6H_4$

Figure 5. Models of: *a*) charge-transfer complex; *b*) transition state; *c*) reaction products.

Exposure to monochromatic light of wavelength 405 or 436 nm changes the mechanism of conversion of the charge-transfer complexes and initiates complete transfer of an electron from donor to acceptor with formation of radical-ion species recorded by electron-spin resonance[191–198]. Under the influence of a light quantum the tetranitromethane molecule, by capturing the electron from the donor, passes into an unstable radical-anion, which then breaks down into a trinitromethanide anion and a nitro-radical $\cdot NO_2$. The radical-cation $D^{\dot{+}}$ is stabilised as the nitrocarbonium cation D^+NO_2 by addition of the paramagnetic nitro-radical:

$$D + C(NO_2)_4 \rightleftarrows D^{\oplus\delta}\cdots\cdots{}^{\ominus\delta}C(NO_2)_4 \xrightarrow{h\nu} D^{\dot{\oplus}} + {}^{\dot{\ominus}}C(NO_2)_4 \rightarrow$$
$$\rightarrow D^{\dot{\oplus}} + {}^{\cdot}NO_2 + \overset{\ominus}{C}(NO_2)_3 \rightarrow D^{\oplus}NO_2 + \overset{\ominus}{C}(NO_2)_3 \ .$$

The subsequent course of the reaction is determined by the changes undergone by the trinitromethanide–nitrocarbonium ion-pair.

A radical-ion mechanism is improbable for the reaction with 1,1-di-*p*-methoxyphenylethylene at 300 K), for photoexcitation by a light quantum in the intermolecular charge-transfer band does not influence the rate of transfer, and no induction period is detected even in the presence of oxygen. One-electron transfer may be possible for the reaction with alkenes, terminating in the synthesis of other products, but this mechanism has not been confirmed experimentally.

The alternative of a free-radical decomposition of the charge-transfer complex, leading to a paramagnetic trinitromethyl radical with a subsequent chain reaction, has also been discussed[193–197]. In the absence of illumination at 300 K and of high concentrations of the initial components, however, paramagnetic species are not directly generated by tetranitromethane for alkenes[198]. The nitro-radical and other paramagnetic species sometimes recorded result from thermal decomposition of the nitronic ester of trinitromethane.

Steric rearrangement of the charge-transfer complex by a free-radical mechanism to reaction products is permissible for the reaction with 1,1-di-*p*-methoxyphenylethylene, but the dipole moment of the transition state will then be determined by that of the $(p\text{-}CH_3OC_6H_4)_2C(CH_2NO_2)\cdot$ radical. Comparison of its dipole moment with that of the transition state (~5 and ~15 D) excludes a chain reaction mechanism under the given conditions.

V. CHEMICAL PROPERTIES

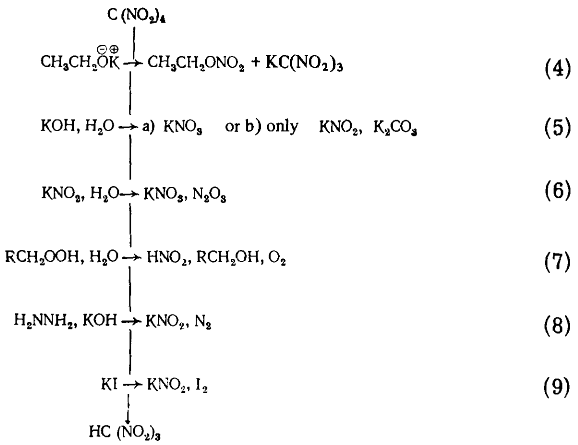
1. Nucleophilic Substitution

The sterically strained arrangement of the four electrophilic nitro-groups in the molecule lowers the activation energy of the carbon–nitrogen bond, enhances the electrophilic character of the carbon atom, usually through the charge-transfer complex stage, and makes it the centre of attack by nucleophilic reagents.

Hantzsch and Rinckenberger[199] found that tetranitromethane is smoothly converted in almost theoretical yield into its salt by the reaction (4) which has remained to the present time the most convenient laboratory method for obtaining trinitromethane (by the action of an alcoholic solution of potassium hydroxide or ethoxide). However, aqueous potassium hydroxide, depending on its concentration, either gives the same results with the formation of potassium nitrate or causes complete degradation to potassium nitrite and carbonate[133,200] (reaction 5). The potassium salt of trinitromethane can be obtained also by the reaction of tetranitromethane with potassium hydroxide dissolved in aqueous glycerol[201].

A patented process of obtaining trinitromethane and its salts is based on the hydrolysis of tetranitromethane in the presence of nitrites of light metals, the consumption of which is diminished by conducting the reaction in the presence of a base—potash, potassium hydroxide, potassium or sodium acetate, etc. (reaction 6).[202] At the same time a detailed kinetic study was made of the reaction of tetranitromethane with hydroxide and nitrite ions[203,204]. The rate-determining stage is formation of a charge-transfer complex in the first case, and in the second case the reaction is of the first order with respect to both tetranitromethane and the nucleophile. Alkyl hydroperoxides are a thousandfold as effective as hydroxide ions in accelerating the reaction[204] (7).

Attempts to obtain the sodium salt of trinitromethane by the action of sodium methoxide on tetranitromethane were unsuccessful[205]. Compounds used as denitrating agents were potassium sulphite and phosphite, hydrazine[206], hydrogen peroxide[24], potassium hexacyanoferrate(II),[207] potassium iodide[208], etc. The reaction with hydrazine can be used for the quantitative determination of tetranitromethane from the nitrogen evolved (8).[206] Phenylhydrazine in the presence of caustic potash converts tetranitromethane into the potassium salt of nitromethane[201]. The reaction of tetranitromethane with sodium sulphite underlay a method for purifying crude trinitrotoluene by washing it with 3–5% sodium sulphite solution[209]. Iodometric[210] and spectrophotometric[211] methods of determining tetranitromethane are based on its reaction with potassium iodide (9) in aqueous alcohol; overall the reaction has the second order, and the first order with respect to each of the components[211,212].



$$C(NO_2)_4 + CH_3CH_2\overset{\ominus\oplus}{O}K \rightarrow CH_3CH_2ONO_2 + KC(NO_2)_3 \quad (4)$$

$$KOH, H_2O \rightarrow \text{a) } KNO_3 \text{ or b) only } KNO_2, K_2CO_3 \quad (5)$$

$$KNO_2, H_2O \rightarrow KNO_3, N_2O_3 \quad (6)$$

$$RCH_2OOH, H_2O \rightarrow HNO_2, RCH_2OH, O_2 \quad (7)$$

$$H_2NNH_2, KOH \rightarrow KNO_2, N_2 \quad (8)$$

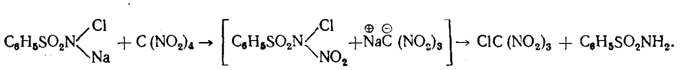
$$KI \rightarrow KNO_2, I_2 \quad (9)$$

$$HC(NO_2)_3$$

The action of lithium, potassium, rubidium, and caesium halides on tetranitromethane in dimethylformamide can be used for the separation of halogenotrinitromethanes[213,214]:

$$C(NO_2)_4 \xrightarrow[-KNO_2]{KX} XC(NO_2)_3$$
$$X = Cl, Br, F.$$

The next two reactions are essentially non-nucleophilic, but yield substitution products. In dimethylformamide and dimethyl sulphoxide tetranitromethane reacts readily with chloramine B to form chlorotrinitromethane via a stage involving *N*-chloro-*N*-nitrobenzenesulphonamide and sodium trinitromethanide[215,216]:



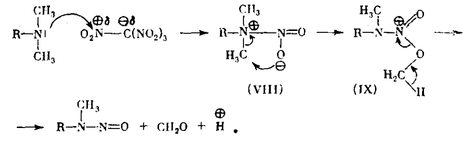
$$C_6H_5SO_2N\genfrac{}{}{0pt}{}{Cl}{Na} + C(NO_2)_4 \rightarrow \left[C_6H_5SO_2N\genfrac{}{}{0pt}{}{Cl}{NO_2} + \overset{\oplus\ \ominus}{NaC}(NO_2)_3\right] \rightarrow ClC(NO_2)_3 + C_6H_5SO_2NH_2.$$

Recent reports[217,218] that a nitro-group in tetranitromethane can be replaced by an alkyl in a medium comprising acetone and Hexametapol or dimethylformamide have aroused interest in connection with a discussion of the reaction mechanism[214,219].

2. Nitrosation of Tertiary Amines

Schmidt[133,220-222] accomplished by means of tetranitromethane the nitrosation of aliphatic and aromatic tertiary amines in pyridine and of ring-halogenated aromatic tertiary amines in acetic acid.

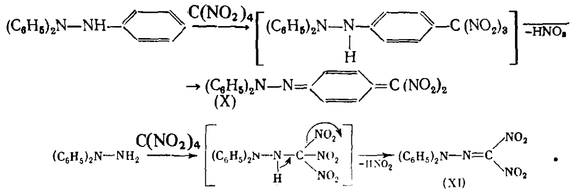
The nitrosation of ethylbenzylamine yields 14% of *N*-nitrobenzylamine and 70% of nitrosoethylbenzylamine[223]. The conversion of tertiary amines into nitrosamines probably involves intermediate formation of a nitroammonium ion (VIII); four-centre transfer leads to rupture of the nitrogen–carbon bond with formation of a nitronic ester (IX), which dissociates into a nitrosamine and an aldehyde[140]:



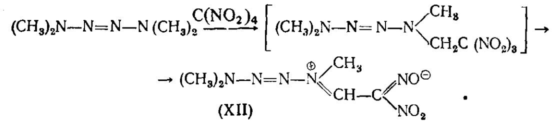
Michler's ketone and *p*-iodo-*NN*-dimethylaniline are probably nitrosated similarly[224]. However, the mechanism of the nitrosation of tertiary amines by tetranitromethane requires further elaboration.

3. *gem*-Dinitromethylation

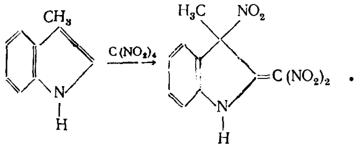
In several cases tetranitromethane acts as a *gem*-dinitromethylating agent as well as an oxidant. Thus with triphenylhydrazine it forms (X),[225] and with *αα*-diphenylhydrazine it gives (XI).[226] In all cases initial trinitromethylation of the nucleophilic compound (as a result of a four-centre transfer) is followed by elimination of one nitro-group, leaving a *gem*-dinitromethylene derivative:



Tetramethyltetrazen is converted into the zwitterion (XII):[227]



With skatole the *gem*-dinitromethylated product contains another nitro-group[228]:



In a brief communication on the reaction of tetranitromethane with cycloalkenes[229] a dinitromethane structure was incorrectly attributed to the main reaction product[230,231].

4. Electrophilic Substitution

Nitroalkanes, *gem*-dinitroalkanes, aromatic hydrocarbons, and arylalkenes having an activated multiple bond undergo mild nitration by tetranitromethane (in an alkaline medium). Mononitroalkanes and *gem*-dinitroalkanes in an alkaline medium yield trinitroalkanes[232,233]:

$$RCH_2NO_2 \xrightarrow{KOH} RCH{=}NOOK \xrightarrow[-KC(NO_2)_3]{C(NO_2)_4} RCH(NO_2)_2 \xrightarrow{KOH}$$
$$\rightarrow RC(NO_2)_2{=}NOOK \xrightarrow[-KC(NO_2)_3]{C(NO_2)_4} RC(NO_2)_3 .$$

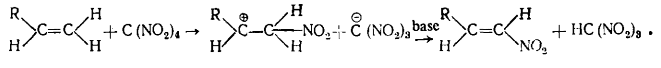
Several aromatic hydrocarbons undergo nitration in the presence of strong nucleophilic reagents (caustic alkalis, pyridine); e.g. *p*-cresol is nitrated to *m*-nitro-*p*-cresol[234], and naphthalene to 1-nitronaphthalene[183]. *NN*-Dimethyl-*p*-toluidine (in a neutral medium) forms with tetranitromethane a salt of trinitromethane and *m*-nitro-*NN*-dimethyl-*p*-toluidine, which on treatment with alkali is converted into *m*-nitromethyl-*p*-toluidine[234]. In the absence of alkali *N*-alkylcarbazoles are nitrated in the ring, slowly but with high yields[235]; nitration is considerably accelerated by ultraviolet irradiation. Kinetic investigation of the nitration of *para*-substituted phenols[236] in water and in 95% ethanol showed in both cases the second order with respect to the phenol, the limiting stage being dissociation of the charge transfer-complex.

The nitration of tyrosine at pH 8.0 by tetranitromethane to 3-nitrotyrosine stimulated intensive research on proteins containing tyrosine residues[237-248]. Alkaline nitration has been used to obtain nitro-derivatives of azulenes. Thus an 85% yield of 1-nitro-2,4,8-trimethylazulene was isolated from the nitration of 2,4,8-trimethylazulene in the presence of pyridine[249,250]. Cyclopenta[*c*]thiapyran gave with tetranitromethane the corresponding mononitro-derivative[251].

Arylalkenes in which the double bond was conjugated with the ring were nitrated by Schmidt[222,234] in the presence of pyridine and acetone to the corresponding β-nitroalkenylarenes: e.g.

$$CH_3OC_6H_4CH{=}CH_2 \xrightarrow[\text{pyridine}]{C(NO_2)4} CH_3OC_6H_4CH{=}CHNO_2 \ .$$

Nitration of the same arylalkenes in methyl and ethyl alcohols yielded α-alkoxy-β-nitro-compounds[222]. Unconjugated arylalkenes[222], containing the double bond in the allyl position with respect to the ring, are not nitrated under these conditions. Bülich[181], Patterson[140], and Titov[252,253] assumed that the reaction with arylalkenes takes place by an ionic mechanism; the formation of conjugated nitroalkenes on alkaline nitration was regarded as the result of consecutive reactions involving the base—electrophilic addition to the alkene of the nitronium cation produced by heterolytic breakdown of tetranitromethane, formation of an ion-pair, nucleophilic attack by the base on the nitrocarbonium cation, and its stabilisation, with elimination of a proton, as a conjugated nitroalkene:

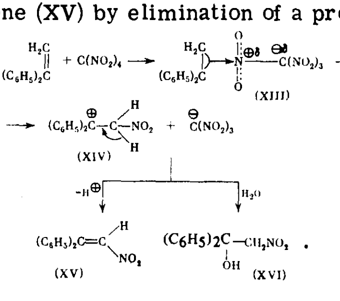


In the absence of bases addition products are formed by tetranitromethane with such alkenes, e.g. p-anethole[254].

5. Electrophilic Addition

A comprehensive investigation by Perekalin and Altukhov[263,264] of the reaction with substituted alkenes, arylalkenes, vinyl ethers, and dienes revealed fundamentally new reaction paths. For example, several conjugated nitroalkenes were obtained by the action of tetranitromethane on alkenes in a neutral medium.

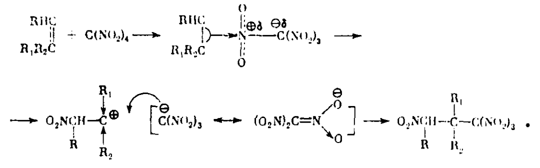
Tetraphenylethylene does not react owing to steric hindrance of the double bond and the absence of ethylenic hydrogen atoms; the behaviour of 1,1-diphenylisobutene is similar. In these cases interaction between the hydrocarbon and tetranitromethane ceases at the charge-transfer complex stage, with equilibrium displaced towards the initial components. When one or two phenyl groups attached to the same ethylenic carbon atom in tetraphenylethylene are replaced by hydrogen atoms, steric hindrance is diminished, and reaction with tetranitromethane becomes possible. Thus triphenylethylene[255], 1,1-diphenylethylene[255,256], and 1,1-di-p-methoxyphenylethylene[257] in the absence of basic catalysts form conjugated nitroalkenes via the stage of a charge-transfer complex (XIII), which is converted by electrophilic incorporation of a nitronium cation into a nitrocarbonium cation (XIV) (with the trinitromethanide anion as gegenion), and this is stabilised as the nitroalkene (XV) by elimination of a proton:



Intermediate formation of an ion-pair is confirmed, in particular in the case of diphenylethylene, by isolation from the reaction medium of the corresponding nitro-alcohol (XVI) resulting from attack by the hydroxide ion (in the presence of water) on the nitrocarbonium cation. The presence of an ion-pair has been established also by electron spectroscopy in the action of tetranitromethane on 1,1-di-p-dimethylaminophenylpropene[258]. Shielding of the cationoid carbon atom by the two phenyl groups excludes nucleophilic addition of the trinitromethanide anion. The reactivity of 1,1-diarylethylenes with tetranitromethane increases with the electron-donating power of the double bond.

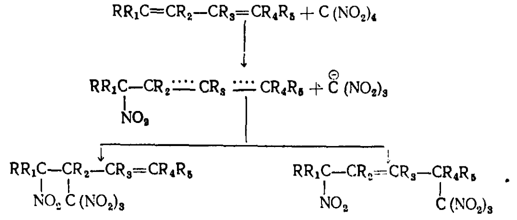
The action on alkenes in which the number of bulky phenyl rings has diminished at least to one at each carbon atom forming the double bond is more complicated and results in different final products depending on steric and electronic factors (alkyl groups adjoining the double bond and substituents in the aromatic ring). This is due to diminished steric hindrance at the cationoid carbon atom of the intermediate nitrocarbonium cation, which enables it to interact with the ambident trinitromethanide anion at its two reaction centres—an oxygen atom of the nitro-group (C-alkylation) and the carbon atom (C-alkylation)—depending mainly on the nature of the nitrocarbonium cation and to some extent on the character of the solvent.

Accumulation of nucleophilic groups in the initial alkene enhances the basic character of the double bond, increases the degree of delocalisation of the positive charge on the electrophilic centre of the nitrocarbonium cation, and causes it to react at the carbon atom of the trinitromethanide anion—the reaction centre having a smaller electron density—to form C-alkylated products (nitrotrinitromethylation)—1,1,1,3-tetranitroalkanes:



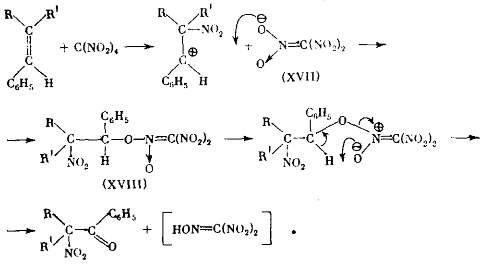
R- Ar ; R_1, R_2- Alk

Such behaviour is exhibited by styrene derivatives alkylated at the α and β positions[259,260], arylcyclenes[231,260], and styrene derivatives *para*-substituted by electron-donating groups[254,257,261–266]. Dienes containing two or more methyl groups also undergo C-alkylation by tetranitromethane[267–269]:



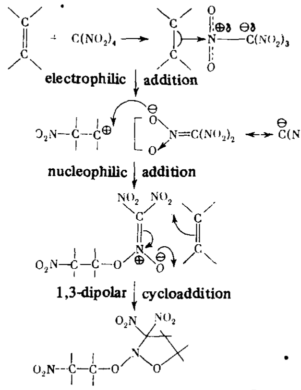
The conjugated nitrocarbonium cation formed reacts with the trinitromethanide anion either at the 1,2-positions (2,3-dimethylbutadiene) or at the 1,4-positions (2-methylpenta-2,4-diene, 2,4-dimethylpenta-1,3-diene, and 2,5-dimethylhexa-2,4-diene) to form the corresponding tetranitroalkenes.

In the action of tetranitromethane on less basic unsaturated compounds the nitrocarbonium cation (XVII) appears with a considerable positive charge on the electrophilic carbon atom, and the trinitromethanide anion adds to it at the nitro-oxygen atom having the greatest electron density (*O*-alkylation) with formation of an unstable nitroalkyl ester of aci-trinitromethane (XVIII), which is a 1,3-dipole capable of 1,3-addition of a second molecule of the alkene. However, the presence even of one substituent (phenyl or alkyl) in the β-position of the initial alkene, i.e. in the styrene derivative, makes addition of a second molecule of the alkene sterically impossible, and the resulting nitronic ester (XVIII) undergoes thermal decomposition by an intramolecular redox reaction with formation of α-nitro-ketones and dinitroformaldehyde oxime[255,257,264,270]:



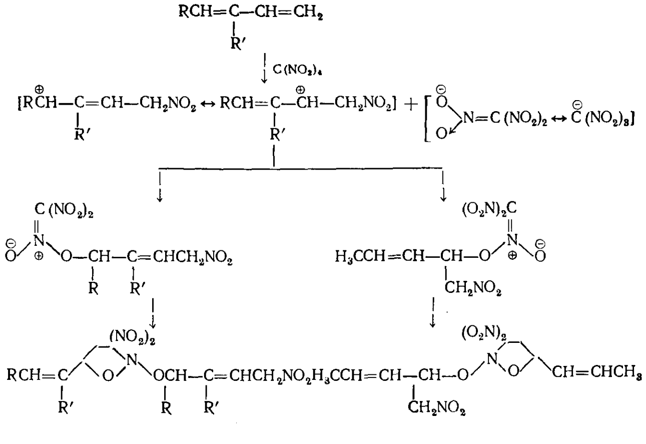
An indispensable condition for this process to occur is the presence of an α-hydrogen atom in the nitroalkyl ester (XVIII). The unstable oxime decomposes with the liberation of nitrogen sesquioxide, which nitro-nitrosates the initial alkene (yield 3–22%) and oxidises part of the oxime to trinitromethane. Formation of nitro-ketones is often accompanied by more fundamental degradative oxidation processes. Thus tetranitromethane reacts with *p*-methoxy-ββ-dimethylstyrene[256] and with cyclohexene[270] in the absence of a solvent to give anisic and adipic acids respectively. Carboxylic acids were obtained also[160] by heating tetranitromethane with elaidic acid, stilbene, and but-2-ene. Tetranitromethane smoothly oxidises quinol to quinone, and dimethylaniline to Crystal Violet[147,151].

The action of tetranitromethane on unsaturated compounds containing adjacent to the double bond less bulky groups than phenyl (ethylene, its alkyl derivatives independently of the number and arrangement of the groups about the double bond, and also allyl and vinyl ethers), as well as styrene derivatives unsubstituted at the β-position, leads to the synthesis of 3,3-dinitroisoxazolidine derivatives[231,255,257,261,270–274]:



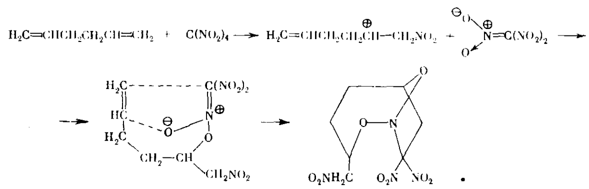
Formation of the charge-transfer complex and the ion-pair is followed by nucleophilic attack on the nitrocarbonium cation by an oxygen atom of the trinitromethanide anion to give a reactive ester of aci-trinitromethane. This reacts synchronously with a second molecule of the initial alkene, by a mechanism of 1,3-dipolar cycloaddition, to give the 3,3-dinitroisoxazolidine derivative.

With $\pi\pi$-conjugated systems tetranitromethane forms 3,3-dinitroisoxazolidine derivatives containing multiple bonds in the side-chains, as a result of 1,4-addition to butadiene and isoprene, and 1,2-addition to pentadiene; cycloaddition takes place only at the less substituted multiple bond in a diene[267,269]:

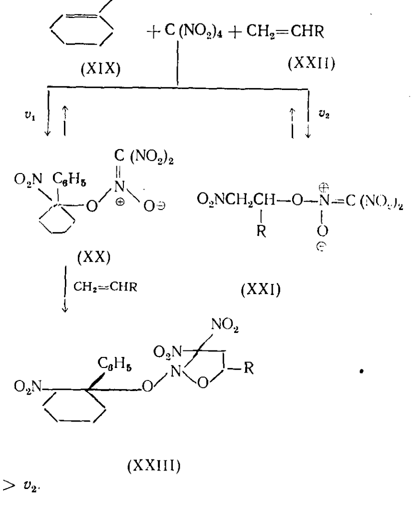


R, R'=H; R=H, R'=CH₃ .

As a result of intramolecular cyclisation of the intermediate nitronic ester the reaction with hexa-1,5-diene yields a bicyclic isoxazolidine[267]:



Intermediate formation of nitronic esters of trinitromethane is supported by the controlled synthesis of substituted 3,3-dinitroisoxazolidines (of mixed composition) from tetranitromethane and two different alkenes[259,275,276]. Initially the reaction of tetranitromethane with the sterically hindered but more nucleophilic alkene (XIX) produces the nitronic ester (XX) more rapidly than the nitronic ester (XXI) is formed from the less nucleophilic and also sterically less hindered alkene (XXII); the ester (XX) then reacts with the sterically unhindered alkene (XXII), and is stabilised as the substituted dinitroisoxazolidine (XXIII) (the steric hindrance in (XIX) makes reaction of the alkene (XIX) with the nitronic esters (XX) and (XXI) impossible):



$v_1 > v_2$.

6. Acceptance of Radicals

A considerable number of studies have been made on the homolytic decomposition of tetranitromethane by the action of bases, ultraviolet radiation, or γ-rays.

Electron-spin resonance has shown that reaction with strong nucleophiles (benzidine, *NNN'N'*-tetramethylbenzidine[277], and sodium 2,4,6-tri-t-butylphenoxide[278]) begins with the appearance of charge-transfer complexes and concludes with formation of the corresponding radical-anions, which break down into anions and radicals, e.g. the 2,4,6-tri-t-butylphenoxyl radical and the trinitromethanide anion. Similar results were obtained for the action of tetranitromethane on 1,3-dicarbonyl compounds in alkaline media or under ultraviolet irradiation[279,280].

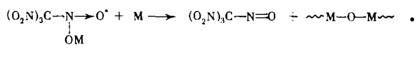
A radical-dianion of trinitromethane has been detected in the electrochemical reduction of tetranitromethane in dimethylformamide, acrylonitrile, and water[281]. Photolysis of tetranitromethane by ultraviolet radiation in water and methanol[282], in the presence of ketones, $\alpha\beta$-unsaturated ethers and esters, cyclohexene, styrene[283], and benzene derivatives[198], generates $NO_2\cdot$ radicals. The trinitromethyl radical was not detected owing to its great activity and rapid interaction with the solvent. The fragmentation of tetranitromethane has been studied mass-spectroscopically[284,285].

The radiolysis of tetranitromethane by γ-rays at 77°K is accompanied[286] by its breakdown into $\cdot NO_2$ and $\cdot C(NO_2)_3$ radicals. The latter is represented in the e.s.r. spectrum by a sextet having relative intensities 1 : 3 : 6 : 6 : 3 : 1. However, it is not recorded in solution or in the presence of organic compounds[286-288]. The main products of radiolysis in aqueous solution by cobalt-60 γ-rays are the $\cdot NO_2$ radical and trinitromethane in yield $I = 3.75/100$ eV, which is increased by the presence of small quantities of organic compounds (ethanol, benzene, ethyl acetate, etc.)[289-295].

Being an acceptor of radicals, tetranitromethane effectively slows down the polymerisation and the cross-linking of polymers initiated by radiation[296,297] or by free radicals[298-303]. The "spin echo method" has shown for methyl methacrylate as example that retardation of polymerisation is favoured by increasing the number of nitro-groups in the polynitroalkane[301]:

$$CH_3NO_2 < CH_3COO\,(CH_2)_2C\,(NO_2)_2(CH_2)_2COOCH_3 <$$
$$< CH_3CH\,(NO_2)_2 < (O_2N)_3C\,(CH_2)_2COOCH_3 < C\,(NO_2)_4 \ .$$

Tetranitromethane inhibits the radical polymerisation of methyl methacrylate in the presence of benzoyl peroxide owing to the formation of relatively inactive free radicals causing chain termination; at the same time it accelerates decomposition of the benzoyl peroxide[304]:



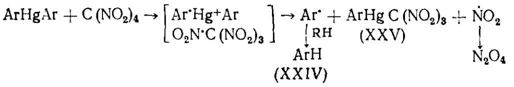
$$(O_2N)_3C\underset{\textstyle OM}{-N}\!\!\longrightarrow O^{\cdot} + M \longrightarrow (O_2N)_3C{-}N{=}O + \sim\!\sim M{-}O{-}M\sim\!\sim \ .$$

M - Monomer

As a strong acceptor of electrons, tetranitromethane initiates ionic polymerisation. Thus oxetan is polymerised by a cationic mechanism on the addition of 1,1-diphenylethylene and tetranitromethane[256], which is explained by formation of a nitrocarbonium cation as initiator. Vinylcarbazole is polymerised similarly[305-307] in the presence of methyl methacrylate (1–10%) and tetranitromethane. Donor–acceptor interaction between tetranitromethane and cyclic sulphides[308] promotes ring opening and subsequent polymerisation.

The rules found in the reactions of tetranitromethane with unsaturated compounds are general in character and can be extended to the reactions of these alkenes with trinitromethane derivatives containing other substituents (chloro-, bromo-, and iodo-trinitromethane, trinitroacetonitrile, trinitroacetic ester). Replacing a nitro-group by a different residue changes the direction of addition of the trinitromethanide anion to the carbonium cation and hence the proportions of the reaction products. For example, the tendency of the intermediate trinitromethanide anion to *C*-alkylation is greater with bromo- and iodo-trinitromethane[309-311].

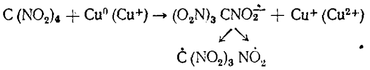
Since the Review was presented for publication several interesting communications have appeared on the chemistry of tetranitromethane. It reacts similarly with mercury and tin aryls[312] and with phenylmagnesium chloride[313]; with aryl derivatives of mercury the products are the corresponding aromatic hydrocarbons (XXIV) and the aryltrinitromethylmercury (XXV). The oxidation involves a stage of one-electron transfer followed by formation of an aryl radical and its interaction with the solvent (RH):



$$ArHgAr + C\,(NO_2)_4 \rightarrow \begin{bmatrix} Ar^{\cdot}Hg^{+}Ar \\ O_2N^{\cdot}C\,(NO_2)_3 \end{bmatrix} \rightarrow \underset{\underset{(XXIV)}{ArH}}{\overset{}{Ar^{\cdot}}\big\downarrow{\scriptstyle RH}} + \underset{(XXV)}{ArHg\,C\,(NO_2)_3} + \underset{N_2O_4}{\dot{N}O_2\big\downarrow} \ .$$

The detection of $\cdot NO_2$, $\cdot C(NO_2)_3$, and radicals from nucleophiles in the photolysis of tetranitromethane and in its dark reaction with various nucleophilic reagents supports the hypothetical one-electron mechanism in several of its reactions with nucleophiles and provides information on possible modes of breakdown of the tetranitromethane radical-anion in the matrix[314].

The reaction with metallic copper probably also involves a stage of one-electron transfer, with formation of the radical-anion (XXVI), which breaks down into the $\cdot C(NO_2)_3$ and $\cdot NO_2$ radicals[315]:



$$C\,(NO_2)_4 + Cu^0\,(Cu^+) \rightarrow (O_2N)_3\,CNO_2^{\dot{-}} + Cu^+\,(Cu^{2+})$$
$$\swarrow\ \searrow$$
$$\dot{C}\,(NO_2)_3\ \ N\dot{O}_2 \ .$$

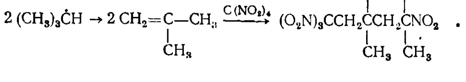
(XXVI)

Discussion has continued on the mechanism of the formation of trinitroethane from iodomethane and tetranitromethane[316]. The mechanism

$$S + C\,(NO_2)_4 \rightarrow \underset{(XXVII)}{S \cdots\cdot NO_2 \cdots\cdot C\,(NO_2)_3} \xrightarrow{CH_3I} CH_3C\,(NO_2)_3 + S + INO_2$$

has been suggested for the process in a polar solvent. In the complex (XXVII) formed by tetranitromethane with the solvent, which was isolated and examined by physicochemical methods, polarisation of a carbon–nitrogen bond facilitates attack by iodomethane and the formation of 1,1,1-trinitroethane.

The formation of 3,3,5-trimethyl-1,1,1,5-tetranitrohexane by the thermolysis of trimethylacetic acid in tetranitromethane is attributed[317] to conversion (which requires further evidence) of the t-butyl radical into isobutene and telomerisation of the latter involving tetranitromethane:



$$2\,(CH_3)_3\dot{C}H \rightarrow 2\,CH_2{=}\underset{\textstyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow{C\,(NO_2)_4} (O_2N)_3CCH_2\overset{\textstyle CH_3}{\overset{|}{\underset{\textstyle CH_3}{\underset{|}{C}}}}CH_2\overset{\textstyle CH_3}{\overset{|}{\underset{\textstyle CH_3}{\underset{|}{C}}}}NO_2 \ .$$

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Industrial Applications of Free and Immobilised Enzymes

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The methods for the preparation and purification of immobilised enzymes are briefly reviewed and examples are given of the utilisation in industry (mainly not in the food industry) of enzymes such as amylases, proteinases, cellulases, glucose oxidase, glucose isomerase, lipase, and invertase. Various procedures for the immobilisation of enzymes are described. The principal aspects of catalysis by immobilised enzymes are examined, particularly from the standpoint of the stability of the enzymes, reaction kinetics, and the influence of diffusion. Certain examples of the employment of enzymes incorporated in fibres are presented (hydrolysis of penicillin, cleavage of milk lactose, and isomerisation of glucose). The bibliography includes 65 references.

CONTENTS

In recent years, enzymatic reactions have found extensive applications in chemical and pharmaceutical industries. The present review is concerned with examples of the industrial (in the main not in the manufacture of food products) employment of enzymatic reactions, achieved both with the aid of enzymes in solution and with the aid of immobilised enzymes, which is particularly important in connection with their increasing value as industrial catalysts[†].

I. ENZYMES IN SOLUTION

For technical and economic reasons, microbiological systems are the most important source of enzymes used in industry. The relevant micro-organisms are grown in surface or bulk-phase cultures. Aqueous extracts containing enzymes are then subjected to further treatment by various methods for the purpose of concentration, partial purification, stabilisation, and conversion of the enzyme material into the finished commercial product.

Extracellular enzymes are normally used, which makes it possible to isolate them relatively simply, and does not require the disruption of cells, although nowadays this can be easily done with the aid of modern homogenisers[1]. The scheme for the isolation of enzymes illustrated in Fig. 1 is usually employed[2].

When necessary, preservatives are added, for example, toluene, organic acids, phenolic compounds, quaternary ammonium salts, or sodium fluoride. Enzymes are precipitated by adding to the purified solutions or liquid concentrates, under strictly controlled conditions, precipitants such as organic solvents (acetone, ethanol), inorganic salts (sodium or ammonium sulphate, disodium hydrogen phosphate), or macromolecular compounds [poly(ethyleneglycol)]. The precipitated enzyme, isolated by filtration or centrifugation, is dried at atmospheric pressure or *in vacuo* at a low temperature, and the solid concentrate is ground to the required particle size. The concentrate obtained contains, apart from the required enzyme, other proteins and also moisture, carbohydrates, and inorganic salts[3]. Since the cost of the preparation is usually more important for commercial purposes than high purity, it is

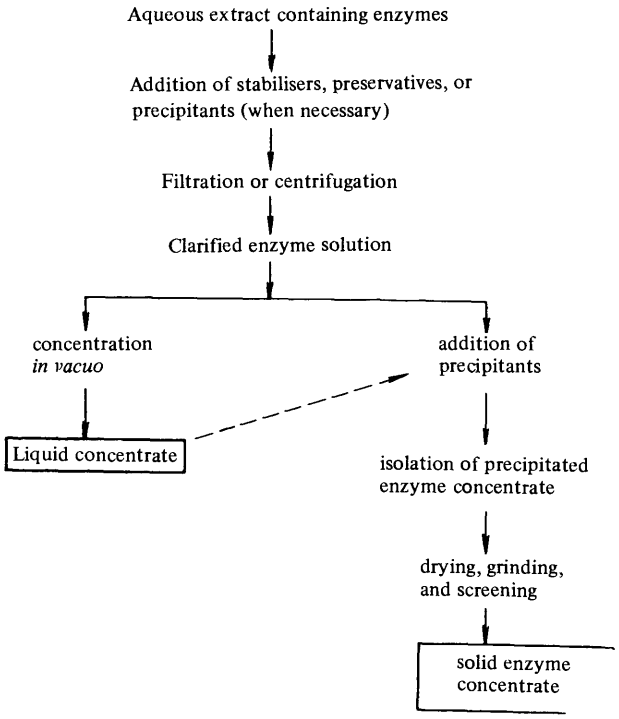


Figure 1. Scheme for the isolation of enzymes.

[†] At the present time, this problem is dealt with most completely in the collected volume edited by I. V. Berezin, "Immobilizovannye Fermenty" (Immobilised Enzymes), Izd. Moskov. Gos. Univ., Moscow, 1975 (a). The kinetic and thermodynamic aspects of catalysis by immobilised enzymes are described by I. V. Berezin, A. M. Klibanov, and K. Marinek, Uspekhi Khim., 44, 17 (1975) [Russian Chemical Reviews, No. 1 (1975)].

not subjected to further purification. However, in certain cases the presence of contaminating enzymes or other substances in the preparation is undesirable if they can have an unfavourable influence on products or processes. Thus the enzymes used for special analytical purposes, certain pharmaceutical processes, and research must be carefully purified[2]. In the manufacture of high-purity enzymes, it is necessary to employ special methods, for example fractional precipitation, differential adsorption and elution[4], chromatography[5], electrophoresis[6], dialysis[7], crystallisation, and lyophilisation.

Table 1. Some industrial enzymes and their microbiological sources[8].

Source	Enzyme	Microorganism
Mould fungi	amylases	*Aspergillus oryzae*
	glucosidases	*Aspergillus flavus*
	proteinases	*Aspergillus niger*
	pectinases	*Aspergillus niger*
	glucoseoxidase	*Penicillium notatum*
	catalase	*Aspergillus niger*
Bacteria	amylases	
	proteinases	*Bacillus subtilis*
	penicillinase	
Yeast	invertase	*Saccharomyces cerevisiae*
	lactase	*Saccharomyces fragilis*

Table 1 lists the commercial enzymes manufactured mainly from various strains of mould fungi, bacteria, and yeast[8]. The most important examples of such enzymes are amylase, certain other carbohydrases, proteinases, glucose oxidase, and pectinase. Methods involving bulk-phase (immersed) cultures are used for their manufacture.

In writing the review of the applications of enzymatic processes in solution in "non-food" industry, the author found that, apart from the manufacture of starch and detergent powders (which will be considered in greater detail in view of their commercial importance), enzymes are used in textile, paper, leather, pharmaceutical, and other branches of industry.

In the textile industry, bacterial amylases are used both for the preparation of modified starch adhesives and for the removal of adhesives from fabrics. Preparations of bacterial amylases, which retain their activity at much higher temperatures than amylases from moulds, have to a larger extent replaced malt and pancreatin. In the paper industry, certain bacterial amylases are used to modify starch for coating paper. Proteinases from *Bacillus subtilis*[9] are employed in the manufacture of tanned leather to remove hair and largely for the softening of leather after tanning by the proteolytic decomposition of gelatin formed from collagen. Such treatment enhances the protective properties and improves the structure of leather[10]. Proteinase preparations should also find future applications as depilatory agents (preparations for the removal of hair) in cosmetics[11].

Mould or pancreatic amylases, proteinases, and lipases and mould cellulases are used as digestion-promoting agents. Steptokinase, trypsin, and other proteinases have found applications in the treatment of wounds and as anti-inflammatory or fibrinolytic agents. Among hydrolytic enzymes, invertase (catalysing the hydrolysis of sucrose to glucose and fructose), used in the preparation of highly concentrated invert sugar syrups and for special purposes, for example for the preparation of soft kinds of chocolate, is of considerable industrial interest. In contrast to the sucrose obtained by acid hydrolysis, enzymatically inverted sucrose does not have an undesirable taste and colour caused by decomposition products (for example, furfural). Of the two possible enzymes hydrolysing sucrose, only β-fructofuranosidase is used. In this case, the centre of attack is the fructose end of the sucrose molecule. This intracellular enzyme, obtained from yeast (usually from *Saccharomyces cerevisiae*), retains its catalytic properties at temperatures of 65–70°C and has the maximum activity at pH 4.5. The purification of invertase by the removal of the majority of impurities increases the sensitivity of the enzyme to physical damage[12]. Unpurified preparations containing small amounts of other enzymes (catalase, hexokinase) are therefore usually employed.

Amylases are extracellular enzymes hydrolysing starch molecules to dextrins and a set of compounds with lower molecular weights consisting of glucose units. They are divided into two classes: endoamylases and exoamylases. Endoamylases act at random on the $1 \rightarrow 4$ linkages in starch, liberating certain reducing groups and forming dextrins with various chain lengths. The $1 \rightarrow 6$ linkages, , which are the branching points in amylopectin and glycogen, are not attacked under these conditions. Exoamylases attack polysaccharides only from the non-reducible terminal groups. They can either cleave each linkage with formation of glucose only (amyloglucosidases) or they can rupture alternate bonds with formation of maltose (β-amylases, which are given this name because the maltose obtained has the β-configuration).

Amyloglucosidases from *Aspergillus niger* are capable of hydrolysing both $1 \rightarrow 4$ and $1 \rightarrow 6$ glucoside linkages in oligosaccharides, but in the latter case the rate of reaction is much lower[13].

Table 2. Microbial amylases*.

Properties	Bacteria		Mould fungi		Other sources	
	solubilisation	saccharification	*Rhizopus*	*A. oryzae* or *A. niger*	*Endomycopsis*	*Oospora*
Thermal stability, °C	65–90	55–70	50–65	55–70	35	50–70
pH stability	4.8–10.6	4.0–7.8	5.4–7.0	4.7–9.5	6.0–7.5	6.0–10.5
Optimum pH	5.4–6.0	4.8–5.2	3.6	4.9–5.2	5.4	5.6
Activity/mg	1800	1190	475	980	760	970
Adsorption on starch	++	—	+	+	+	+
Stabilisation by Ca^{2+} ions	+	—	—	+	?	+
Effect on starch:						
maximum degree of hydrolysis, %	35	70	48	48	90	37
principal product	dextrin, maltose	glucose, maltose, maltotriose	maltose	maltose	glucose	dextrin, maltose
Effect on maltose	—	—	—	—	+	—
Effect on phenylmaltose	—	+	+	+	+	—

*According to data of Dr. J. Fukumoto.

Microbiological α-amylases are obtained either from moulds (mainly *Aspergillus orizae*) or from bacteria (mainly from *Bacillus subtilis*). All the known sources of amylases are listed in Table 2.[13] Commercial α-amylases, obtained from various bacteria and moulds, are characterised by different temperature and pH optima, different stabilities, and different extents to which they decompose starch. In view of its high thermal stability, bacterial α-amylase from thermophilic strains of

Bacillus subtilis can be used to solubilise starch. For this purpose, it is added to the doughy mass of the non-gelatinised starch grains (preferably from potatoes or sweet potatoes), which proceed to the gelatinisation stage and are mixed in the reactor[14]. Industrial processes using glucoamylase from surface *Rhizopus* cultures have been devloped in Japan[15]. Japanese investigators have also suggested that bulk-phase cultures of *Endomyces* strains be used for the preparation of glucoamylase[16]. Processes for the preparation of glucoamylase from *Aspergillus* in immersed cultures have been developed in the USA. This method gives higher yields. The enzyme from *Aspergillus* has excellent properties—a high temperature optimum, a higher stability, and a wider pH range in which it retains its activity.

All commercial glucoamylase preparations must be completely freed from transglucosidase, which is responsible for the formation of small amounts of oligosaccharide impurities, particular isomaltose, which hinder the manufacture of glucose. Several methods have been proposed whereby it is also possible to reduce the content of transglucosidase in glucoamylase preparations: (a) special cultures have been developed, which do not produce transglucosidase; (b) the unpurified enzyme is treated with agents which remove transglucosidase [these include clay minerals[17], sulphonated alcohols[18], $Mg(OH)_2$,[19] and acids[20]]; ion-exchange resins[21] etc. are also employed.

Amylolytic enzymes are used mainly in the manufacture of starch syrups (concentrated aqueous solutions of starch hydrolysates) and crystalline glucose (dextrose). The employment of suitable combinations of α- and β-amylases, amyloglucosidases, isoamylases, or maltases makes it possible to obtain an infinite variety of starch hydrolysis products and hence syrups with any desired properties, for example with a maltose content exceeding 80%.[22]

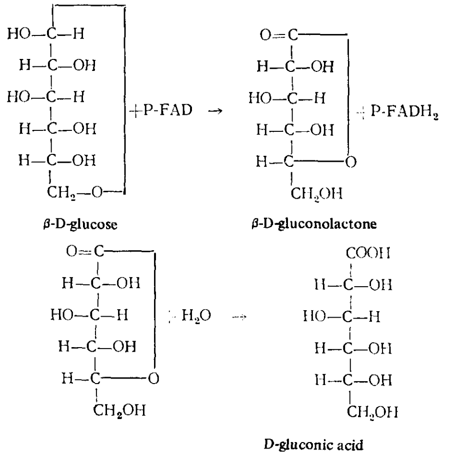
Another interesting enzyme catalysing the conversion of glucose into fructose, is glucose isomerase obtained from certain *Streptomyces* strains and bacteria. Depending on the temperature, the degree of conversion can reach approximately 50%. Since fructose is sweeter than glucose, sweeter syrups can be obtained in this way[14].

Another class of hydrolytic enzymes which are of industrial importance consists of proteinases. They can be of animal origin, for example trypsin, which is obtained from bovine pancreas as a side product after the extraction of insulin and has extensive pharmaceutical applications. Other proteinases are of plant origin, for example ficin, papain, or bromelain, and are mainly used as agents for tenderising meat. Proteinases can be obtained by microbiological methods, with the aid of both mould fungi and bacteria; several species of bacteria are normally employed—such as *Bacillus subtilis*, *Aspergillus niger*, and *Aspergillus oryzae*.

Microbiological proteinases are divided into three groups: acid, neutral, and alkaline[9]. Acid proteinases, which originate mainly from moulds (*Aspergillus*, *Rhizopus*) and are most active in pH range 2–5, are insensitive to the action of compounds with thiol groups, substances forming chelates with metals, and heavy metals, and catalyse the hydrolysis of many peptide linkages. Neutral proteinases are zinc-containing metalloenzymes which are therefore deactivated by chelating agents. The optimum conditions for these enzymes are pH 7–8 and a temperature in the range 45–50°. They do not exhibit esterase activity and mainly cleave peptide linkages of the following type: His-Leu, Ala-Leu, Tyr-Leu, Gly-Phe, and Phe-Phe.

Alkaline proteinases constitute the most important group, since they are widely used in combination with detergents for the removal of stains of protein origin, for example, blood, casein, etc. The most familiar enzymes of this group are subtilisins[9], for example subtilisin *Novo* or subtilisin *Carlsberg* from various *Bacilli* or strains of *Bacillus subtilis*. Alkaline proteinases are active over a wide pH range, from 6 to 11, the maximum activity being shown at pH 9.5–10.5. They exhibit a high esterase activity and cleave peptide linkages of several types.

Proteinases are also used in small amounts in dry cleaning, for the isolation of silver from used photographic film, and for the preparation of protein hydrolysates. Yet another enzyme, namely glucose oxidase, an FAD-dependent aerobic dehydrogenase, has found extensive industrial applications. It converts glucose into gluconic acid with simultaneous formation of equimolar amounts of hydrogen peroxide via the following reactions:



$$\text{P-FADH}_2 + O_2 \rightarrow \text{P-FAD} + H_2O$$

(Here P-FAD = glucose oxidase).

The microbiological source of this enzyme is *Penicillium notatum* and particularly *Aspergillus niger*. The intracellular enzyme from *A.niger* has an optimum in the pH range 4.0–6.5. The commercial enzyme contains catalase, which facilitates its industrial application. Glucose oxidase is used to remove oxygen from preserved non-alcoholic beverages, mayonnaise, and fruit juices, and also for the removal of glucose from eggs before drying.

Catalase, which decomposes hydrogen peroxide to water and oxygen, is used in the manufacture of cheese in order to decompose hydrogen peroxide residues after cold sterilisation, in the manufacture of foam rubber (foam plastics) and porous cement, and to accelerate the bleaching of fur and bird feathers.

Lipase, one of the hydrolytic enzymes, is contained in pancreatin and is produced by many micro-organisms. It is used commercially as an agent promoting digestion, in enzymatic dry cleaning apparatus, for the elimination of waste, and for the decomposition of fats to the fatty acids constituting the basis of ordinary soap[11].

Cellulases are new industrial carbohydrases. The cellulase complex is a mixture of extracellular enzymes (mainly from *Aspergillus niger* or *Trichoderma viridae*)[23] containing, firstly, an enzyme which acts non-specifically, hydrolysing highly oriented solid celluloses (C_1) and, secondly, a multicomponent fraction of $\beta(1 \rightarrow 4)$glucanases (called C_X) both of the exo-type (these remove single glucosidic units from the non-reducible ends of the cellulose chain) and of the endo-type, which yield cellulodextrins, and, thirdly, β-glucodimerases, which act on glucose β-dimers, for example cellobiose. The employment of the cellulase complex from *Trichoderma viridae* made it possible to hydrolyse pretreated cellulose free from lignin to give unpurified extracts containing 8% of glucose[23,24]. Later investigations employing cedar sawdust yielded solutions containing more than 20% of glucose[25]. These extracts can be used to manufacture fermentation products or individual cell proteins. Other promising applications of cellulase may be its use for the removal of plant fibres from wool, or as agents promoting digestion, or for enzymatic dry cleaning.

II. IMMOBILISED ENZYMES

The advantages of immobilised enzymes as catalysts have been described in numerous reviews. Their use in chemical catalysis and automatic analysis is based on the possibility of their repeated use in combination with a high selectivity of the catalysis and a low cost of their preparation and purification; in many cases, the reaction volume can also be reduced. For research purposes, immobilised enzymes can be regarded as specific reagents readily removed from the system, which do not contaminate the products obtained. Furthermore, immobilisation makes it possible to increase the stability of enzymes. Artificially immobilised enzymes can be used, like model systems, to investigate the mechanism of the action of enzymes in biological membranes.

For biomedical purposes, enzymes can be used only in the immobilised form, in order to prevent the allergic response by the organism or undesirable interactions between the enzyme and individual components of the organic solutions being treated. Covalently bound enzymes have assumed increasing importance in the isolation of coenzymes and natural enzyme inhibitors by affinity chromatography from unpurified extracts or partly purified solutions.

These varied and attractive possibilities drew the attention of many investigators during the last few years to the investigation of immobilised enzymes. Various methods for the preparation of immobilised systems have been discovered and the activities of the enzymes obtained have been investigated. The theoretical aspects of the kinetics of the action of these enzyme systems are being vigorously studied together with the engineering problems of the construction of reactors using immobilised enzymes.

Immobilisation Methods

In the discussion of the problem of the utilisation of immobilised enzymes as industrial catalysts, we shall consider only relatively cheap carriers and simple methods for the attachment of enzymes.

Four main methods are used to prepare water-insoluble enzymes: (a) physical incorporation (i.e. incorporation into porous materials, whose cavities are bounded by walls impermeable to proteins but allowing the passage into the cavities of substances with low molecular weights). As an example of such carriers, one may quote polyacrylamide or starch gel, microcapsules, and fibrous matrices. (b) Covalent binding of enzymes to organic or inorganic carriers via the reactions of the functional groups of the proteins which are not responsible for catalytic activity. (c) The formation of covalent intermolecular bonds in the interaction of enzymes with the corresponding bifunctional reactants. (d) Adsorption on insoluble matrices (on ion-exchange resins or an inert support, for example as a result of hydrophobic interactions).

A combination of (c) and (d), i.e. adsorption of the protein on an appropriate carrier followed by the formation of intermolecular bonds, is being successfully used. Table 3 presents some of the most important examples of covalent binding.

We shall now consider the advantages and disadvantages of some of the immobilisation methods quoted above.

Table 3. Methods for the covalent binding of enzymes.

Activator	Carrier
Isothiocyanate	Sephadex Enzacryl AA
Azide	CM-cellulose Enzacryl AH
Carbodi-imide	CM-cellulose acrylamide – acrylic acid
Maleic anhydride	ethylene – maleic anhydride copolymer
Diazo-compounds	Enzacryl AA Polystyrene *p*-aminophenylalanine – leucine copolymer
Cyanogen halide	cellulose Sephadex polysaccharide
N-Ethyl-5-phenyl-isoxazolium-3-sulphonate	polyacrylic acid polyglutamic acid CM-cellulose
Trichloro-*s*-triazine	cellulose DEAE-cellulose DE-cellulose
Glutaraldehyde	AE-cellulose nylon
Silane	glass
Bisdiazobenzidine-2,2′-disulphonic acid	collodion

Physical incorporation in the gel. The inclusion of enzymes in gels such as three-dimensionally "cross-linked" polyacrylamide or starch has the advantage that it can be carried out under fairly mild conditions. Here the carrier has a minimal influence on the immobilised enzyme. The absence of covalent bonds between the enzyme and the matrix makes this method applicable, in principle, to any enzyme.

The relative inaccessibility of enzymes to substrates with large molecular weights, the appreciable influence of the diffusion of substrates and products, and the possible losses of the enzyme as a result of its elution from loose network gels must be regarded as disadvantages of the method[26]. An interesting variety of this immobilisation procedure involves enclosure in microcapsules[26] made of thin spherical semipermeable nylon or collodion membranes, which are used mainly for biomedical purposes.

Incorporation in fibrous structures. The method of incorporating enzymes in a fibrous structure developed in our laboratory belongs to the category of physical incorporation method. It involves the preparation of an emulsion by mixing an aqueous solution of the enzyme with a solution of the polymer in a solvent immiscible with water. The emulsion is then forced through thin draw plates into an immiscible liquid, which results in the coagulation of the polymer[28]; the protein is then included in the pores of the moist, coiled synthetic fibre. The pore size can be varied within certain limits by altering the experimental conditions. Fig. 2 presents an electron microscope photograph of a transverse section through the fibre. This "trapping" technique is very simple, can be applied to any proteins, and makes it possible to achieve both the simultaneous incorporation of several different proteins in the matrix and the incorporation of large amounts of a single protein. The purity of the protein does not affect the "trapping" and the method can be used to incorporate individual organelles, cells, or spores. The enzymes incorporated into the matrix by this procedure are protected from the action of microbes and macromolecular substances produced by microbes, for example proteinases.

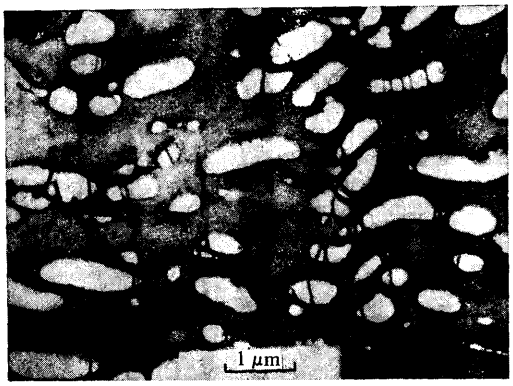


Figure 2. An electron microscope photograph of the transverse section through polymeric fibres.

Evidently in the future it will be possible to increase the stability of the incorporated enzyme by selecting as carriers polymers capable of interacting with the protein globule of the enzyme, stabilising the latter.

Covalent binding. The covalent binding of enzymes to a solid matrix is one of the most widely used methods which have been investigated in detail. Covalent binding has the advantage that the systems obtained are not broken down by altering the pH or the ionic strength and following the addition of the substrate. However, by altering the chemical structure of the enzyme, this method of binding can also alter its reactivity (either as a result of the blocking of the active enzyme centre by the binding reaction or as a result of the involvement in the reaction of the aminoacid residues which participate in the mechanism of enzyme action[26]). Mild conditions, moderate ionic strengths, pH 4–10, and a temperature in the range 0–35°C should obtain during the fixation process. In the course of immobilisation, the active site of the enzyme must be protected by employing covalent blocking agents or by carrying out the reaction in the presence of a substrate or inhibitors. The carrier must be hydrophilic, its porosity must be high, and it is usually necessary to convert it into an active form for reaction with the enzyme. The particle size determines to a large extent the amount of bound enzyme per gram of carrier[29]. An increase of the surface area of the carrier increases the amount of bound enzyme per unit weight and an increase of the number of hydrophilic regions in the polymer also usually increases its binding capacity.

The most suitable centres for the binding of enzyme molecules to the matrix are the terminal amino-groups as well as the lateral amino groups in the lysine residues. The imidazole rings of histidine and the guanidine groups of arginine can participate in the binding process. The acid carboxy-groups of the glutamic and aspartic residues and the C-terminal groups of the proteins can also be effective. Another binding site may be the hydroxyphenyl group of the tyrosine residue, which readily interacts with diazonium reagents.

The immobilisation of enzymes by the formation of intermolecular bonds has been achieved successfully using bifunctional reagents containing two identical functional groups[30] as well as different groups or groups having different reactivities.

It is noteworthy that, although the method of covalent binding of enzymes to suitable carriers does prevent the elution of the enzyme and makes it possible to control the physical properties and particle size of the final product, nevertheless it suffers from certain limitations owing to the sensitivity of many enzymes to chemical modification[30].

Adsorption and methods involving the formation of cross links. Various adsorbents are used to adsorb enzymes—both charged resins and neutral surfaces. The adsorption method does not guarantee complete immobilisation. High concentrations of the salt or substrate increase the rate of desorption of the enzyme. This can be avoided by the formation of intermolecular bonds in proteins after their adsorption. Thus highly active synthetic membranes have been obtained by the formation of a "network" of enzyme molecules adsorbed on collodion[30] or on cellophane membranes[31], or by the formation of a network of enzyme and inactive protein molecules[31].

III. PRINCIPAL ASPECTS OF CATALYSIS BY IMMOBILISED ENZYMES‡

Stability of Immobilised Enzymes

The activity of immobilised enzymes, referred to unit weight, depends on the amount of bound enzyme, which can vary from several milligrams to several grams per gram of carrier, and on the activity of the enzyme itself, which varies from <10% to >100% of the initial value and can actually exceed the activity which the enzyme would have had in the same amount in solution. This depends largely on the various microenvironments of the enzyme on the surface and in the pores of the polymer matrix.

Immobilisation as a rule increases the effective lifetime and thermal stability of the enzyme, but in some cases the opposite effect is also possible: a carrier containing hydrophobic groups to a large extent denatures the protein, while a hydrophilic carrier with a positive or negative charge can influence the stability of the immobilised enzyme as a result of electrostatic interactions between the bound enzyme and the carrier[30]. Proteolytic enzymes are stabilised on immobilisation also because their autolysis is prevented.

The form of the pH dependence on the activity of the immobilised enzyme can differ appreciably from the

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‡ These processes are described in greater detail in Berezin's collective volume (a) and particularly in the review of Berezin et al. (b) (see the footnote to p. 1067).

analogous relation for the same enzyme in solution owing to the changes induced by the polyelectrolyte carrier molecule on the effective acid dissociation constants of the ionisable groups in the active centre of the enzyme. However, more important interactions of the charge–charge type take place between the ionic charges of the substrate or other components in solution and the residual charges on the matrix. If the solution components have a charge opposite to that of the matrix, their concentration near the surface and in the pores of the matrix becomes higher than in the bulk of the solvent; the opposite behaviour is observed for charges of the same sign[33]. For example, the alkaline branch of the pH dependence of the activity of ficin bound to CM-cellulose is displaced by 0.5 of a unit towards higher pH values, since the concentration of protons within the matrix increases owing to their interaction with the field of the negatively charged carboxy-groups[33]. These anomalies disappear at high ionic strengths.

Reaction Kinetics

Enzyme molecules are bound to the carrier as a rule at several points, which leads to the formation of a certain number of cross links and this may hinder the access of the substrate to the bound or shielded enzyme molecule[34]. Another factor influencing the concentration of the substrate in the microenvironment of the active centre of the bound enzyme is diffusion. The particles of the immobilised enzyme in an aqueous suspension are surrounded by an unstirred layer of solution in which a substrate concentration gradient is established[35]. As a result, the saturation of the immobilised enzyme by the substrate takes place at substrate concentrations higher than are required for the saturation of the active centre in solution. This leads to an increase of the effective Michaelis constant. Owing to diffusion, insoluble enzymes exhibit an activity maximum only at fairly high rates of stirring of the solution[36–38]. An example of the favourable influence of diffusion is provided by insoluble polyenzyme systems which are more effective than the individual enzymes in solution, since the product formed in the initial stages does not diffuse instantaneously into the bulk phase but remains on the support at high concentrations, which favours the subsequent stages of the reaction[39].

The effective Michaelis constant for the immobilised enzyme depends on the charge of the matrix if the substrate is also charged[26]: it increases when the signs of the charges of the matrix and the substrate are the same, since the substrate is repelled by the matrix, and decreases for the opposite signs of the charges, since the substrate is then attracted to the matrix and its concentration in the microenvironment of the enzyme is higher than in the bulk of the solution. The Michaelis constant can vary by an order of magnitude and more as a result of these factors.

IV. EXAMPLES OF THE POSSIBLE INDUSTRIAL APPLICATIONS OF IMMOBILISED ENZYMES

Separation of Racemic Mixtures

Numerous studies have been made on the resolution of DL-aminoacids using acylases obtained from microorganisms and pig kidneys.

Chibata and coworkers[40-46] were successful in separating DL-methionine on acylases. There have been reports about the construction of an industrial apparatus with an output of 20 tonnes per month. The author used various methods for the immobilisation of enzymes: (a) ionic adsorption on DEAE-cellulose and DEAE-Sephadex; (b) covalent binding to iodoacetylcellulose; (c) incorporation in a polyacrylamide gel.

Pig kidney acylase, incorporated in fibrous cellulose triacetate, was investigated in the author's laboratory. A highly reactive catalyst was obtained (17 700 μmole h^{-1} per gram of dry fibre at 37°C). Under the conditions of their utilisation at 25°C, the activity of these fibres fell by 25% in 650 h, during which 550 g of L-methionine had been obtained per gram of the dry fibre.

Saccharification of Starch

Lilly and coworkers[47] carried out the covalent binding of amyloglucosidase to DEAE-cellulose with the aid of 2-amino-4,6-dichloro-*s*-triazine. The activity of the resulting enzyme is not specific. However, one should note that it remains constant during 28 days of employment of the enzyme. In a subsequent study[48], it was reported that the protein can be bound in amounts up to 120 mg per gram of carrier and that the activity is approximately 20–30% of that of the initial enzyme. Under the experimental conditions at 50°C, the activity decreases by approximately 30% in 21 days, but at 25°C the enzyme is completely stable.

Smiley and coworkers[49] investigated the ionic binding of amyloglucosidase to DEAE-cellulose. It was found that the activity is 55% of the initial value and remains constant for three weeks at 40°C. Amyloglucosidase from *Aspergillus niger*, incorporated in a polyacrylamide gel[50], has an activity equal to 20% of that of the enzyme in solution, a high thermal stability, and a pH dependence analogous to that for the initial enzyme. The activity persists for approximately 15 h at 60°C and then decreases at a rate of 1.5% per hour. At 50°C the activity is constant for 150 h, after which inactivation begins.

Glucoamylases incorporated in cellulose triacetate fibres were investigated in the author's laboratory[51]. The activity of the insoluble residues in relation to solubilised starch is one tenth of its activity in relation to maltose (possibly because the diffusion of starch molecules, having a high molecular weight, is hindered). The activity of fibres with attached enzyme remains constant during employment for six months in the reaction with maltose at 25°C; in 30% solutions of solubilised starch at 45°C, the activity of the fibres persists for 300 h.

A method has been proposed for the separation of the reaction products from the enzyme and the substrate by means of ultrafiltration membranes[52]. In this case, the enzyme is retained by the membrane and can be used again.

The covalent binding of amyloglucosidase to porous glass was achieved recently[53]. The yield of the binding reaction amounts to 40–60% and may even reach 80%. In the usual method of preparation at 45°C, the average lifetime is 650 days. It has been calculated that 500 columns (with a volume of one cubic foot, i.e. 0.028 m^3) with immobilised glucoamylase would produce sufficient glucose to supply the requirements of the USA.

Numerous studies have been made on the immobilisation of α- and β-amylases. However, the activity of the resulting insoluble derivatives is very low (6–15%) and their stability is unsatisfactory. The immobilisation of pullulanase[54] by covalent binding to the acrylamide–acrylic acid copolymer with the aid of carbodi-imide was reported recently. The degree of binding is 34% and the activity 43%, but the system obtained is unstable.

Isomerisation of Glucose

Glucose isomerase has been immobilised by incorporation in polyacrylamide gel and also as a result of its covalent binding to porous glass. The enzyme proved to be unstable in both cases.

Experiments have been carried out on the incorporation of glucose isomerase in cellulose triacetate fibres[55]. Highly active fibres were obtained and the activity remained virtually constant for two months at 45°C.

The Reduction of Lactose in Milk Products

Immobilised β-galactosidase has been obtained by various investigators. For example, Sharp et al.[56] achieved the covalent binding of the enzyme from *E.coli* to triazinylcellulose derivatives. The stability of the specimens obtained depended markedly on temperature and the presence of possible poisons.

The treatment of milk with immobilised fungal lactase, obtained in the polymerisation of acrylic monomers in the form of spherical pellets, has been reported[57]. The amount of enzyme incorporated is 5.6 mg per gram of carrier. The activity of the specimens is 36%.

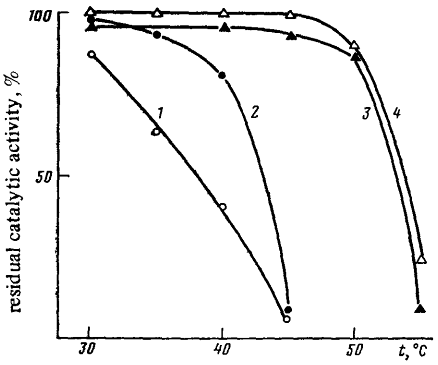


Figure 3. Thermal stability of free yeast β-galactosidase: 1) after incubation for 22 h; 2) after incubation for 6 h; thermal stability of free β-galactosidase from *E.coli*: 3) after incubation for 22 h; 4) after incubation for 6 h.

The properties of yeast β-galactosidase incorporated in cellulose triacetate fibres have been investigated in the author's laboratory[58,65]. The activity of the immobilised β-galactosidase is about 40% of the activity of the free enzyme. Both the free and the immobilised enzymes have an activity maximum at pH 6.0–7.0 (Fig. 3) and 37°C. Milk and pure lactose are hydrolysed at approximately the same rates. The immobilised galactosidase retains the initial activity during employment for 80 days. When very active fibres containing 1500 units of the enzyme per gram of fibre are used, it is possible to hydrolyse milk lactose at low temperatures (5°C) without the risk of altering the organoleptic properties of the treated milk/or of contamination by bacteria (Table 4). The experimental apparatus operating under these conditions demonstrates the possibility of the industrial hydrolysis of milk lactose, which would solve the problem of the elimination of lactose from food products.

Table 4. The influence of the density of filling of columns with cellulose triacetate fibre incorporating yeast β-galactosidase on the hydrolysis of milk lactose.

Amount of fibre, g per ml of column volume	Degree of hydrolysis of milk lactose, %*			
	30 min	60 min	120 min	180 min
0.115	7.75	12.4	23.7	33.7
0.250	7.75	15.0	27.0	38.5
0.400	11.0	14.4	29.8	40.7

*500 ml of milk at 25°C circulated through the column at a rate of 10 litre h^{-1}.

Hydrolysis of Penicillin

Penicillin acylase has been immobilised by covalent binding to derivatives of chloro-*s*-triazinylcellulose[59,60]. It has been shown[59] that the immobilised enzyme has an activity of 25% of the value in solution and retains it during employment for eleven weeks at 37°C. In another investigation[60], the best specimens had an activity between 70 and 120 μmole min^{-1} per gram of carrier, which is 45–80% of the activity of the enzyme in solution.

Penicillin acylase from *E.coli* has been immobilised in the author's laboratory[61] on cellulose triacetate fibres. The activity reaches 40 μmole min^{-1} per gram of carrier and remains constant for 150 days at 37°C. The degree of hydrolysis of penicillin on the enzyme amounts to 98%.

Insoluble specimens with an activity of 110 μmole min^{-1} per gram of carrier have now been obtained in the author's laboratory; with their aid, it is possible to hydrolyse a 12% solution of penicillin in a short time. The synthesis of ampicillin from 6-aminopenicillanic acid and phenylglycine esters has been achieved on the same fibres in a yield of about 70%. Furthermore, the hydrolysis of cephalosporins, which are penicillin derivatives, also takes place in a high yield.

Rearrangements in Steroids

The cells of *Curvularia lunata* trapped in a polyacrylamide gel are used for the 11-β-hydroxylation of Reichstein compounds[62]. The same paper reports the preparation of immobilised *Corynebacterium simplex* cells, which retain the Δ-1-dehydrogenase activity and can be used in columns. However, in both cases the activity of the systems is too low for industrial application.

Consecutive Reactions

The possibility of catalysing a number of consecutive reactions without the isolation of intermediates is of great theoretical and practical interest. Brown et al.[63] investigated the cleavage of glucose by four glycolytic enzymes: hexokinase, phosphoglucoisomerase, phosphofructokinase, and aldolase. The enzymes are incorporated in a polyacrylamide gel and placed in a column in the required sequence.

Mosbach and Mattiasson[39,64] investigated enzyme complexes bound to the same matrix. They obtained[39] β-galactosidase, hexokinase, and glucose-6-phosphate dehydrogenase bound to Sephadex. It was found that a bound complex of this kind has a higher activity than in solution; the authors explained this by the influence of diffusion.

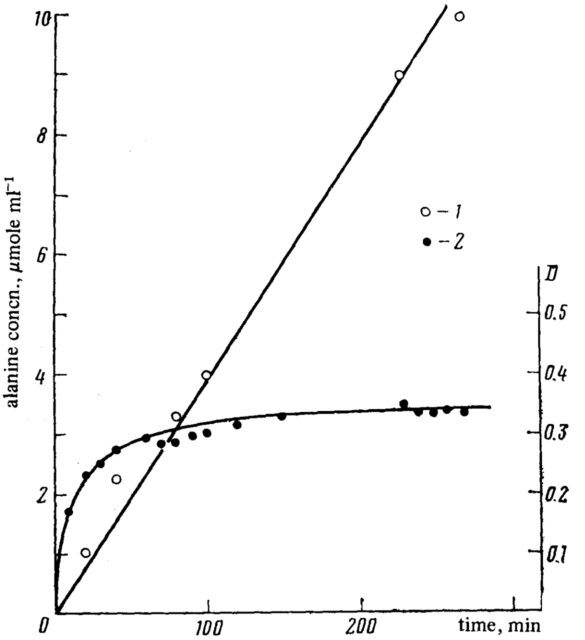
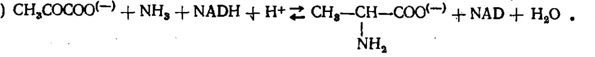


Figure 4. Kinetics of the formation of alanine catalysed by lactate dehydrogenase and alanine dehydrogenase immobilised on fibres: 1) increase of alanine concentration; 2) variation of NADH concentration (D = optical density at 340 nm).

Lactate dehydrogenase and alanine dehydrogenase have been incorporated in fibres in the author's laboratory in order to obtain alanine from lactate and ammonia:

$$(1)\ CH_3CHOHCOO^{(-)} + NAD^+ \rightleftarrows CH_3COCOO^{(-)} + NADH + H^+ \ ;$$

(2) 

$$CH_3COCOO^{(-)} + NH_3 + NADH + H^+ \rightleftarrows CH_3{-}\underset{NH_2}{\underset{|}{CH}}{-}COO^{(-)} + NAD + H_2O \ .$$

Fig. 4 presents typical kinetic curves showing that the concentration of alanine increases linearly, while the concentration of NADH reaches a steady-state value in approximately 100 min. The time required for the attainment of a steady-state concentration is determined by the diffusion of NADH from the microcavities in the fibres to the bulk of the solution.

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Charge Transfer in Complexes of the Donor-Acceptor Type

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Data on the application of physical methods for the estimation of the degree of charge transfer and the nature of charge distribution in complexes of the donor-acceptor type are examined and described systematically. The dipole moment method, infrared spectroscopy, nuclear quadrupole resonance, Mössbauer spectroscopy, X-ray electronic spectroscopy, and quantum-chemical calculations are considered.
The bibliography includes 105 references.

CONTENTS

I. INTRODUCTION

Numerous studies have been devoted to donor–acceptor interaction and the results have been surveyed in a number of reviews and monographs[1-9]. Interpretation of the experimental data in terms of thermodynamic parameters (equilibrium constants, enthalpy, and entropy) does not as a rule present special difficulties. Complexes of different compositions, with different initial components and with different numbers and structures of the latter, can be compared in terms of these parameters, i.e. thermodynamic parameters are to some extent universal. Interpretation of data is somewhat different as regards the structural aspect. In this case, only a comparison is made in terms of spectroscopic data and other characteristics. A general interpretation of the experimental data therefore requires the selection of universal parameters of the same type as in the study of the thermodynamics of the complexes. We believe that such parameters should be charge transfer and the nature of charge distribution in the complex. They are in fact responsible for the changes in structure and physicochemical and chemical properties on complex formation. Unfortunately the available data on charge transfer have not been arranged in an adequately systematic form.

In the present article, an attempt is made to review such estimates of the degree of charge transfer and of the nature of charge distribution in complexes of the π_σ, n_σ, π_v, and nv types. Data on charge transfer in $\pi\pi$ complexes have been adequately described in a number of communications[2,3,5,6] and are not therefore dealt with in the present review.

II. THE EFFECTIVE CHARGE

The concept of the charges of atoms in molecules is fundamental for the description of the electronic structures of chemical compounds. Naturally, complexes constitute merely a specific instance. It is therefore necessary to elucidate the definition of the charge of an atom in an individual molecule and to specify its physical significance.

The simplest and clearest description of the electronic structure of molecules involves the attribution of effective charges to atoms in the molecules†. It is understood that the very concept of the charge depends on the experimental method used to determine it. It is known that an atom in a molecule does not retain its "individuality" and the greater its loss, the less adequate is the description of the observed properties of the molecule in terms of purely atomic characteristics[12]. However, at the present state of development of theoretical chemistry one can employ with some caution the concept of the effective charge of an atom to describe the experimentally observed characteristics[13].

The model of the effective charge presupposes that the entire electronic charge of the atom can be represented by a point charge, coinciding with the nucleus. We shall assume after Mulliken that the electron density resulting from the overlapping of the wave functions of the atoms is shared between them in accordance with their non-equivalence. On the other hand, Levdin began with a basis set of atomic orbitals subjected to preliminary orthogonalisation[12]. There is then no need for assigning the overlap densities to the atoms. In principle, Levdin's definition of the effective charge reflects more satisfactorily the true charge distribution in the molecule, but so far virtually all investigations have been based on the analysis of Mulliken populations. In the present review, we shall therefore also estimate the effective atomic charges by Mulliken's method[2,14,15].

The formation of a complex of the donor–acceptor type is known to be caused by charge transfer from the donor to the acceptor[9]. We shall therefore consider charge transfer in the ground state of the complex and shall confine ourselves to an examination of the simplest wave function of the ground state (ψ_N):

$$\psi_N = a\psi_0(DA) + b\psi_1(D^+A^-). \tag{1}$$

The coefficients a and b in Eqn. (1) characterise the fractions of the structure "without bonds" and of the structure with complete charge transfer. When the ratio b/a is small, the fraction of the state with charge transfer is likewise small and the complex is stabilised mainly by electrostatic forces (dipole–dipole, dipole–induced dipole, ion–dipole, etc.). When b/a is large, the contribution of the charge-transfer state is likewise large and the forces caused by charge transfer can appreciably exceed the usual intermolecular forces.

The coefficients a and b are related by the normalisation condition:

$$\int \psi_N^2 d\tau = 1 \quad \text{or} \quad a^2 + b^2 + 2abS_{01} = 1 \ ,$$

where S_{01} is the overlap integral of the wave functions ψ_0 and ψ_1. Here S_{01} is linked to the overlap integral S_{DA} of the wave functions of the donor (ψ_D) and acceptor (ψ_A) in the following way[9]:

$$S_{01} = \frac{\sqrt{2}\,S_{DA}}{(1 + S_{DA}^2)^{1/2}} .$$

The degree of charge transfer has been defined in different ways by different workers: b^2, $b^2/(a^2 + b^2)$, and $b^2 + abS_{01}$. It follows from estimates of Mulliken populations that the degree of charge transfer is more correctly characterised by the quantity $b^2 + abS_{01}$. For weak complexes, where $b \ll a$, different definitions of charge transfer lead to virtually identical numerical results, but for strong complexes the differences are significant. In all cases, we chose the same definition of the degree of charge transfer in terms of the quantity $\Delta = b^2 + abS_{01}$. The results presented in the Tables have been recalculated in those cases where the authors used other definitions of the degree of charge transfer.

There are many physical methods which make it possible to estimate the transferred charge in complexes and such estimates are based on Mulliken's definition of the charge. The methods include electronic absorption spectroscopy, the dipole moment method, infrared spectroscopy, nuclear quadrupole resonance (NQR), nuclear gamma-resonance (NGR) or the Mössbauer effect, X-ray electronic spectroscopy, and quantum-chemical calculations. Electronic spectroscopy permits the estimation of the coefficients a and b only for very weak complexes and we shall not therefore consider results obtained by this method.

Since the application of such different research techniques leads in essence to an adequate estimation of the degree of charge transfer, it is of interest to compare the transferred charges and the nature of their distribution in complexes, obtained by different methods for the same compounds.

III. THE DIPOLE MOMENT METHOD

One of the first methods used to investigate charge transfer in complexes was the dipole moment method. This method is very sensitive to changes in the charge distribution in the molecule, partial transfer of electron density from the donor to the acceptor resulting therefore in the generation of a very significant additional dipole moment.

Briegleb[3] obtained an expression for the dipole moments of the complex (μ_N):

$$\mu_N = a^2\mu_0 + b^2\mu_1 + abS_{01}(\mu_1 + \mu_0),$$

where $\mu_0 = \mu_D + \mu_A$ is the vector sum of the dipole moments of the non-interacting donor and acceptor for a specified configuration of the complex and μ_1 is the dipole moment of the complex with complete charge transfer. For convenience, the expression can be transformed as follows:

$$\mu_N - \mu_0 = (b^2 + abS_{01})(\mu_{DA} + \mu_D' + \mu_A' - \mu_D - \mu_A), \tag{2}$$

---

† An attempt was made recently to formulate a general quantum-mechanical definition of the charge of an atom in a molecule and of bond orders[10,11]. This approach employs the technique of projection operators and electron density operators. However, despite its advantages (the generality of the procedure, the invariance of the results with respect to any orthogonal transformations, etc.), the results are difficult to interpret. For example, all the atomic charges are found to be negative, etc.[10]

where μ_{DA}, μ'_D, and μ'_A are the respective dipole moments of the donor–acceptor bond and of the components corresponding to complete charge transfer. It is seen from Eqn. (2) that the additional dipole moment $\mu_N - \mu_0$ is due to the dipole moment of the donor–acceptor bond $(b^2 + abS_{01})\mu_{DA}$ and the changes in the dipole moments of the initial components as a result of complex formation $(b^2 + abS_{01})(\Delta\mu_D + \Delta\mu_A)$. It follows from Eqn. (2) that $b^2 + abS_{01}$, i.e. a quantity close to the Mulliken population, is a characteristic of the degree of charge transfer determined from dipole moments.

In practice, the degree of charge transfer is usually calculated in the following way: the dipole moments of the initial components are substracted from the observed dipole moment and the resulting difference is attributed to the dipole moment of the donor–acceptor bond. The latter is divided by er, where r is the distance between the directly coordinated atoms, and the transferred charge is thus obtained. It is seen from Eqn. (2) that this estimate is approximate and the calculated degree of charge transfer is closer to the true value the smaller the changes in the dipole moments of the components as a result of complex formation. This has been described in adequate detail in a monograph[9]. Here one need only mention that the dipole moment is a quantity characterising the charge distribution in the molecule of the complex as a whole, and not in its individual fragments. Because of this, the method of dipole moments cannot in principle yield the true degree of charge transfer and the difference between the true value and the value determined from the vector scheme will be greater the more effective the transfer of the influence of complex formation from the coordinating centres to other fragments of the molecules.

Table 1. The experimental dipole moments (μ) and the degrees of charge transfer ($b^2 + abs_{01}$) in the complexes $I_2.L$.[3,16,18]

Complex	μ_D, D	μ_N, D	S_{01}	$\Delta = (b^2 + abS_{01})$, e
$I_2 \cdot C_5H_5N$	2.21	4.50	0.1	0.25
$I_2 \cdot (CH_2)_4S_2$	0	2.15	0.1	0.11
$I_2 \cdot (CH_3)_2S$	1.40	3.62	0.1	0.12
$I_2 \cdot (CH_3)_4CSN_2$	4.70	7.52	0.1	0.18
$I_2 \cdot (CH_3)_4CON_2$	3.66	5.20	0.1	0.09
$I_2 \cdot (CH_2)_4O_2$	0	1.30	0.1	0.06
$I_2 \cdot (CH_3)_2SO$	3.85	5.59	0.02	0.18
$I_2 \cdot (C_8H_{17})_3PO$	4.10	6.21	0.02	0.21
$I_2 \cdot C_5H_5NO$	4.22	6.66	0.02	0.24
$I_2 \cdot 4\text{-}CH_3C_5H_4NO$	4.73	7.43	0.02	0.26
$I_2 \cdot (C_6H_5)_3AsO$	5.25	8.87	0.02	0.37

The most accurate results in studies on charge transfer should be obtained for complexes with non-polar components. In this case, the dipole moments of the donor, μ_D and μ'_D, are zero. Furthermore, for halogens μ_A is equal to zero; assuming that the charge is transferred to σ antibonding orbitals, one can assume that μ'_A is likewise zero. The additional dipole moment of the complex is then caused only by charge transfer. Thus the degree of charge transfer in the complex $I_2.C_6H_6$ found from the values of μ_N derived from two different sources[3,5] is 0.03 e or 0.08 e. The results of studies on charge transfer between the non-polar acceptor I_2 and polar donors are presented in Tables 1 and 2.

The Tables show that the degree of charge transfer varies within wide limits depending on the strength of the donor. In the complexes $TiCl_4.L$ (Table 2), the contribution of μ_A to the dipole moment of the complex is zero because of the square structure of $TiCl_4$ in the complexes. The main uncertainty into the calculation of the degree of charge transfer is therefore introduced by the change of the dipole moment of the donor. In the complexes $SnCl_4.L$ (Table 2), an additional error is introduced into the calculation of the transferred charge by the change in the dipole moment of the Sn–Cl bond. It is at present difficult to estimate the accuracy of the determination of the degree of charge transfer—the uncertainty in the contributions of the above factors makes it virtually impossible to make such an estimate.

Table 2. The dipole moments (μ), the degrees of charge transfer ($b^2 + abS_{01}$), and the heats of formation of donor–acceptor bonds (ΔH) for complexes of the $n\sigma$ and nv types[9].

Complex	μ_N, D	μ_D, D	μ_{DA}, D	r_{DA}, Å	$\Delta = b^2 + abS_{01}$, e	$-\Delta H$, kcal mole^{-1}
$I_2 \cdot (C_2H_5)_2O$	1.90	1.21	1.4	2.60	0.11	4.3
$I_2 \cdot C_5H_{10}O$	2.82	1.63	1.8	2.60	0.14	4.9
$I_2 \cdot C_4H_8O$	3.00	1.70	2.0	2.60	0.16	5.3
$I_2 \cdot (C_6H_5)_2S$	1.99	1.56	0.4	2.78	0.03	0.3
$I_2 \cdot (C_3H_5)_2S$	3.64	1.44	2.0	2.78	0.15	4.6
$I_2 \cdot (C_6H_5CH_2)_2S$	3.78	1.38	2.2	2.78	0.16	4.8
$I_2 \cdot (i\text{-}C_8H_{17})_2S$	4.72	1.63	3.1	2.78	0.23	7.4
$I_2 \cdot (i\text{-}C_7H_{15})_2S$	4.90	1.63	3.4	2.78	0.25	8.1
$I_2 \cdot (C_2H_5)_2S$	4.62	1.60	3.1	2.78	0.23	7.8
$I_2 \cdot (C_3H_7)_2S$	4.90	1.55	3.4	2.78	0.25	8.1
$I_2 \cdot (C_4H_9)_2S$	5.00	1.57	3.6	2.78	0.27	7.6
$I_2 \cdot (C_5H_{11})_2S$	5.34	1.58	3.8	2.78	0.28	7.0
$I_2 \cdot (C_8H_{17})_2S$	5.07	1.58	3.5	2.78	0.26	7.4
$I_2 \cdot C_4H_8S$	5.49	1.87	3.9	2.78	0.29	10.0
$I_2 \cdot (C_6H_{11})_2S$	5.44	1.60	4.0	2.78	0.30	10.5
$I_2 \cdot (C_6H_5CH_2)_3N$	2.80	0.65	1.1	2.30	0.10	2.3
$I_2 \cdot C_5H_5N$	5.70	2.02	2.7	2.30	0.24	7.5
$I_2 \cdot C_9H_7N$	5.70	2.25	2.5	2.30	0.23	7.1
$I_2 \cdot C_4H_9NH_2$	6.07	1.40	3.4	2.30	0.31	8.4
$SnCl_4 \cdot C_6H_5SC_2H_5$	4.20	1.48	0.9	2.27	0.07	2.0
$SnCl_4 \cdot (C_6H_5CH_2)_2S$	4.77	1.38	1.5	2.27	0.12	3.8
$SnCl_4 \cdot (C_3H_7)_2S$	6.49	1.55	3.3	2.27	0.27	12.9
$SnCl_4 \cdot (C_4H_9)_2S$	6.71	1.57	3.5	2.56	0.28	12.6
$SnCl_4 \cdot (C_8H_{17})_2S$	6.79	1.58	3.6	2.56	0.29	11.9
$SnCl_4 \cdot (i\text{-}C_8H_{17})_2S$	3.76	1.63	0.4	2.56	0.03	0.4
$SnCl_4 \cdot CH_3CN$	7.63	3.40	1.2	2.20	0.11	7.0
$SnCl_4 \cdot C_6H_5CN$	8.40	3.90	1.5	2.20	0.14	6.1
$TiCl_4 \cdot C_6H_5CN$	7.08	3.90	3.1	2.13	0.50	11.5
$TiCl_4 \cdot (C_4H_9)_2O$	3.67	1.22	2.5	2.18	0.24	6.0
$TiCl_4 \cdot (C_8H_{17})_2O$	3.83	1.22	2.6	2.18	0.25	6.3
$TiCl_4 \cdot C_5H_{10}O$	4.52	1.87	3.1	2.18	0.30	12.0
$TiCl_4 \cdot C_4H_8S$	4.54	1.71	4.1	2.47	0.34	12.0
$TiCl_4 \cdot (C_2H_5)_2S$	4.66	1.58	4.3	2.47	0.36	11.5
$BF_3 \cdot (CH_3)_2O$	4.35	1.25	1.7	1.54	0.23	13.7
$BF_3 \cdot C_4H_8O$	5.68	1.70	2.6	1.54	0.35	18.8

The method involving the estimation of charge transfer from the enthalpies of complex formation ($-\Delta H$) may be regarded as a "derivative" of the dipole moment method. The linear relation $-\Delta H = 35.3\ \mu_{DA}/er_{DA}$ makes it possible to determine the transferred charge from the known value of ΔH (Table 2). For small and moderate charge transfers, this equation yields fully acceptable results. However, for large values of $-\Delta H$ and μ_{DA}, the coefficient of the relation between $-\Delta H$ and μ_{DA} will be different and cannot be used to determine the degree of charge transfer. For example, in the study of complexes of SO_3 with ethers[18], the coefficient μ_{DA}/er_{DA} proved to be 79.96.

IV. INFRARED SPECTROSCOPY

Infrared spectroscopy is one of the main methods used to estimate the degree of charge transfer. The degree of charge transfer can be estimated from the changes in the force constants of the halogen–halogen bonds for σ acceptors, and metal–halogen bonds for v acceptors with the aid of the force constants of the donor–acceptor bonds and from the relative changes in the stretching vibration frequencies on complex formation. One should note that the most correct values should be obtained using force constants, since in this case there is no reduced mass effect. However, owing to the difficulties in the calculation of the force constants of bonds, estimates of the degree of charge transfer from changes in the frequencies of the stretching vibrations have become most common, and in almost all studies of this kind complexes of σ acceptors are considered. The formation of complexes by v acceptors as a rule leads to a decrease of the stretching vibration frequencies of the metal–halogen bonds, but the degree of charge transfer cannot be estimated unambiguously from the relative shift of these frequencies, since the formation of complexes by v acceptors entails a change in the hybridisation of the central atom and hence a change in the parameters of the metal–halogen bonds (the amount of ionic character, the amount of double bond character, etc.), which must naturally be reflected in their frequencies.

Table 3. The degree of charge transfer in complexes of σ acceptors according to infrared spectroscopic data*.

Complex	Δ_1, e	Δ_2, e	Δ_3, e	Complex	Δ_1, e	Δ_2, e	Δ_3, e
$Cl_2 \cdot C_6H_6$	—	0.08	0.06	$ICl \cdot (C_6H_5)_2$	—	0.17	0.11
$Br_2 \cdot C_6H_6$	—	0.13	0.09	$ICl \cdot CH_3CN$	—	0.24	0.15
$Br_2 \cdot CH_3C_6H_5$	—	0.15	0.10	$ICl \cdot C_5H_5N$	0.46	0.64	0.42
$Br_2 \cdot ClC_6H_5$	—	0.09	0.07	$ICl \cdot 3\text{-}CH_3C_5H_4N$	0.41	0.69	0.39
$Br_2 \cdot C_6H_5COC_6H_5$	—	0.08	0.06	$ICl \cdot 4\text{-}CH_3C_5H_4N$	0.46	0.77	0.43
$Br_2 \cdot C_6H_5C_6H_5$	—	0.08	0.06	$ICl.2,6\text{-}(CH_3)_2C_5H_3N$	0.44	0.77	0.43
$Br_2 \cdot C_5H_5N$	0.36	0.76	0.42	$ICl.2,3\text{-}(CH_3)_2C_5H_3N$	0.46	0.81	0.45
$Br_2 \cdot CH_3CN$	—	0.08	0.06	$ICl.2,4\text{-}(CH_3)_2C_5H_3N$	0.52	0.90	0.50
$Br_2 \cdot (C_2H_5)_3N$	—	0.78	0.44	$ICl \cdot (CH_3)_3N$	—	0.92	0.51
$I_2 \cdot C_6H_6$	—	0.09	0.07	$ICl \cdot Cl_2CHSCH_3$	—	0.41	0.24
$I_2 \cdot CH_3C_6H_5$	—	0.11	0.08	$ICl \cdot ClCH_2SCH_3$	—	0.47	0.27
$I_2 \cdot 1,2\text{-}(CH_3)_2C_6H_4$	—	0.13	0.09	$ICl \cdot (C_6H_5)_2S$	—	0.56	0.32
$I_2 \cdot C_5H_5N$	0.21	0.53	0.24	$ICl \cdot CH_3SC_6H_5$	—	0.71	0.40
$I_2 \cdot 2\text{-}CH_3C_5H_4N$	--	0.39	0.23	$ICl \cdot (CH_3)_2S$	—	0.99	0.55
$I_2 \cdot 4\text{-}CH_3C_5H_4N$	—	0.39	0.23	$ICl \cdot CH_3SC_2H_5$	0.53	0.92	0.51
$I_2 \cdot (CH_3)_3N$	0.43	0.51	0.30	$ICl \cdot (C_2H_5)_2S$	0.53	0.92	0.51
$I_2 \cdot (C_2H_5)_3N$	—	0.31	0.18	$IBr \cdot C_6H_6$	0.09	0.11	0.08
$I_2 \cdot CH_3CN$	—	0.08	0.06	$IBr \cdot CH_3C_6H_5$	0.10	0.15	0.10
$I_2 \cdot Cl_2CHSCH_3$	—	0.15	0.10	$IBr \cdot 1,2\text{-}(CH_3)_2C_6H_4$	0.10	0.15	0.10
$I_2 \cdot ClCH_2SCH_3$	—	0.36	0.21	$IBr \cdot CH_3CN$	0.12	0.17	0.11
$I_2 \cdot (C_6H_5)_2S$	—	0.39	0.23	$IBr \cdot C_5H_5N$	0.36	0.57	0.35
$I_2 \cdot CH_3SC_6H_5$	—	0.43	0.25	$IBr \cdot (CH_3)_3N$	—	0.61	0.34
$I_2 \cdot (CH_3)_2S$	0.30	0.54	0.31	$IBr \cdot (C_2H_5)_3N$	—	0.60	0.34
$I_2 \cdot CH_3SC_2H_5$	0.30	0.54	0.31	$IBr \cdot Cl_2CHSCH_3$	—	0.39	0.23
$I_2 \cdot (C_2H_5)_2S$	0.33	0.52	0.30	$IBr \cdot ClCH_2SCH_3$	—	0.49	0.28
$I_2 \cdot (t\text{-}C_4H_9)_2S$	—	0.56	0.32	$IBr \cdot (C_6H_5)_2S$	—	0.58	0.33
$ICl \cdot C_6H_6$	—	0.19	0.12	$IBr \cdot CH_3SC_6H_5$	—	0.94	0.52
$ICl \cdot CH_3C_6H_5$	—	0.19	0.12	$IBr \cdot (CH_3)_2S$	—	0.86	0.48
				$IBr \cdot CH_3SC_2H_5$	—	0.90	0.50

*The degrees of charge transfer Δ_1, Δ_2, and Δ_3 have been calculated by Eqns. (4), (3), and (5) respectively.

In complexes formed by halogens, the stretching vibration frequencies of the halogen–halogen (X–X′) bonds are also reduced[19–28]. Mulliken[2] links such changes to the degree of charge transfer by the relation

$$\Delta = b^2 + abS_{01} \simeq \frac{8}{3} \cdot \frac{\Delta\nu}{\nu_1}, \tag{3}$$

where $\Delta\nu = \nu_1 - \nu_0$ is the difference between the vibration frequencies of the X–X′ bond in the free halogen molecule and in the molecule bound in the complex. The third column of Table 3 lists the degrees of charge transfer Δ_2 obtained from the literature data using Eqn. (3). In order to estimate $b^2 + abS_{01}$, one can also use the change in the stretching vibration frequencies of the bonds of the donor molecules. However, in this case the coefficient of $\Delta\nu/\nu_1$ is unknown. Furthermore, complex formation results in changes in the stretching vibration frequencies of many bonds in donor molecules and it is impossible to select a single vibration as a criterion for the estimation of the degree of charge transfer.

As mentioned above, the most accurate degrees of charge transfer are obtained when the force constants $f_{X\text{-}X'}$ of the halogen–halogen bonds are used. Thus, following Mulliken[2], many workers employ $f_{X\text{-}X'}$ to estimate the contribution of the dative structure to the electronic ground state of the complexes[19,22,29,30]. The relation for the estimation of the degree of charge transfer can then be represented in the form

$$\Delta = b^2 + abS_{01} = \frac{f^0_{X\text{-}X'} - f_{X\text{-}X'}}{f^0_{X\text{-}X'}}, \tag{4}$$

where $f^0_{X\text{-}X'}$ and $f_{X\text{-}X'}$ are the force constants of the halogen–halogen bond in the free halogen molecule and in the complex. The second column of Table 3 lists the degrees of charge transfer Δ_1 calculated by Eqn. (4) from the literature data both by Person and coworkers[22,23] and in some cases by the present authors. Comparison of the transferred charges obtained from Eqns. (3) and (4) shows that the agreement between them is poor. Bearing in mind that Eqn. (4) gives a better estimate of the degree of charge transfer than Eqn. (3), we attempted to find another coefficient of $\Delta\nu/\nu_1$ in Eqn. (3) from the correlation between $\Delta\nu/\nu_1$ and $(f^0_{X\text{-}X'} - f_{X\text{-}X'})/f^0_{X\text{-}X'}$. The degrees of charge transfer in halogen complexes were determined from the resulting relation:

$$\Delta = b^2 + abS_{01} \simeq 1.42\,\Delta\nu/\nu_1 + 0.02 \quad . \tag{5}$$

The fourth column of Table 3 shows that the degree of charge transfer Δ_3 calculated by Eqn. (5) is closer to the values obtained from the ratio of the bond force constants and, furthermore, that Eqn. (5) holds satisfactorily for different types of complexes—both $\pi\sigma$ and $n\sigma$.

Analogous results are also obtained in the study of complexes of chlorine and olefins. The degrees of charge transfer have been calculated[31] by Eqn. (3). However, the results (based on the donor properties of olefins) appear to be too high, since the transferred charges are the same as in the stronger $n\sigma$ complexes of iodine and amines. On the other hand, the estimates by Eqn. (5) lead to more acceptable values (Table 4).

The degree of charge transfer can also be estimated from the force constants f_{DA} of the donor–acceptor bonds. Here one usually begins with the hypothesis that f_{DA} is determined solely by the contribution of the dative structure[9]:

$$\Delta = b^2 + abS_{01} \approxeq f_{DA}/f^0_{DA}, \tag{6}$$

where f^0_{DA} is the force constant of the donor–acceptor bond in the purely dative structure. The simultaneous application of Eqns. (4) and (6) leads to the expression[9]

$$f^0_{DA} = \frac{f_{DA} f^0_{X\text{-}X'}}{f^0_{X\text{-}X'} - f_{X\text{-}X'}}. \tag{7}$$

f^0_{DA} calculated by Eqn. (7) from the experimental values of f_{DA} and $f^0_{X-X'}$ for halogen complexes[22] proved to be 2.5×10^5 dyn cm^{-1}, i.e. close to the values of f_{DA} for the most stable donor–acceptor complexes of Group III metal halides, where the contribution of the structure with charge transfer plays the dominant role. An estimate of the transferred charge[9] showed that it amounts to (0.4–0.8) e for complexes of aluminium halides[29] and (0.2–0.4) e for complexes of iodine with various donors[22].

Table 4. The degrees of charge transfer in the $\pi\sigma$ complexes of Cl_2 with olefins[31]*.

Complex	$\nu^{c}_{Cl-Cl'}$ cm^{-1}	$\Delta\nu/\nu_1$	Δ_1, e	Δ_2, e
$Cl_2\cdot H_2C{=}CH_2$	520	0.039	0.07	0.10
$Cl_2\cdot H_2C{=}CHCl$	526	0.031	0.06	0.08
$Cl_2\cdot H_3CCH{=}CH_2$	500	0.076	0.13	0.20
$Cl_2\cdot CH_3CH_2CH{=}CH_2$	500	0.076	0.13	0.20
$Cl_2\cdot H_2C{=}CH(CH_2)_4CH_3$	500	0.076	0.13	0.20
$Cl_2\cdot (CH_3)_2C{=}CH_2$	495	0.085	0.14	0.23
$Cl_2.(CH_3)_2C = CHCH_3$	480	0.113	0.18	0.30
$Cl_2.H_2C = CHCH_2Cl$	518	0.042	0.08	0.11

* Δ_1 and Δ_2 are the degrees of charge transfer calculated by Eqns. (5) and (3) and ν^{c}_{Cl-Cl} is the stretching vibration wavenumber of the Cl–Cl bond in the complex.

Interesting results were obtained for complexes of v acceptors[32]. The authors calculated the force constants of the metal–halogen bonds in the complexes $BX_3.NCCH_3$ (X = F, Cl, or Br). Table 5 presents the force constants of the metal–halogen bonds calculated using symmetrical (A) and asymmetric (E) vibrations and it also includes the degrees of charge transfers obtained by the authors. One should note that the large differences between the degrees of charge transfer in the complex $BF_3.NCCH_3$ calculated from the force constants of the symmetrical and asymmetric vibrations cast doubt on the validity of the calculation of the force constants in this case.

Table 5. The degrees of charge transfer in the complexes of BX_3 with CH_3CN. [32]

Compound	Force constant, mdyn Å^{-1}		$\Delta=b^2+abS_{01}$, e	
	A	E	A	E
BF_3	8.82	7.82	—	—
$BF_3\cdot NCCH_3$	6.49	3.85	0.26	0.51
BCl_3	4.63	4.19	—	—
$BCl_3\cdot NCCH_3$	3.32	3.24	0.28	0.23
BBr_3	3.64	2.80	—	—
$BBr_3\cdot NCCH_3$	2.94	2.45	0.19	0.12

V. NUCLEAR QUADRUPOLE RESONANCE AND MÖSSBAUER SPECTROSCOPY

Nuclear quadrupole resonance (NQR) began to be used in the study of charge transfer comparatively recently. The method makes it possible to estimate the degree of charge transfer in complexes and the nature of charge distribution in the components. The changes in the quadrupole interaction constants (QIC) or the electric field gradient (EFG) on complex formation are directly related to the changes in electron density at all the atoms of the interacting molecules. As a result of this, the extent of the change in the charges of the quadrupole nuclei can be estimated from the changes in the QIC (or EFG). For atoms whose nuclei do not have a quadrupole moment in the ground state, one can employ the Mössbauer method. Mössbauer spectra also make it possible to obtain the values of the QIC and in addition the isomeric shifts δ, which is related to the population of the s orbitals of the atom investigated. However, the population of the s orbitals is difficult to estimate quantitatively from the isomeric shift, since the shielding of the s electrons by p and d electrons exerts a major influence on δ.

Relations between the EFG (Δq_A), on the one hand, and the degree of charge transfer b^2 and the nature of charge distribution c^2_{At} in the acceptor molecule on the other have been obtained[33] using the Mulliken theory:

$$\Delta q_A=\frac{b^2}{1+S^2_{DA}}\sum_t c^2_{At}q_t, \qquad (8)$$

where S_{DA} is the overlap integral of the wave functions ψ_D and ψ_A, c^2_{At} the electron density of the t atomic orbital of the electron-accepting molecular orbital, and q_t the contribution to the EFG at the given nucleus of the acceptor molecule due to a single electron in this atomic orbital.

For diatomic halogens and interhalogen compounds, Eqn. (8) simplifies:

$$\frac{\Delta\nu}{\nu}\simeq\frac{\Delta q_{zz}}{q_{zz}}=-\frac{b^2}{2(1-S^2_{DA})}, \qquad (9)$$

where Δq_{ZZ} is the change in the EFG on complex formation and $\Delta\nu$ the change in the NQR frequency of the halogen atom. It is seen from Eqn. (9) that Δq_{ZZ} is directly proportional to the degree of charge transfer. An increase in σ-electron density in the molecule leads to an increase of the population of the p_Z orbital of the halogen atom, which decreases the EFG and the NQR frequency. One should note that in this approximation account is taken of the change in the charge only of the molecule, disregarding the overlap integral of the wave functions of the donor and the acceptor.

For the more involved complexes of v acceptors, it is impossible to obtain an analytical expression giving an estimate of the degree of charge transfer. Quantitative estimates of this kind can be made only with the aid of specific calculations.

We shall examine certain quantitative results for complexes of halogens and interhalogen compounds. Complexes of bromine with π and n donors have been most fully investigated[34–37]. The observed low-frequency shifts are small and lie in the range 0.01–0.04%. Table 6 presents the NQR frequencies of ^{81}Br and the degrees of charge transfer calculated by Eqn. (9). Complexes of chlorine with π and n donors have been less thoroughly studied[38]. In these complexes, low-frequency shifts are also observed and the degrees of charge transfer can be estimated by Eqn. (9) (Table 6). The degree of charge transfer for complexes of both Br_2 and Cl_2 is evidently insignificant and agrees well with the results obtained by other methods[9].

The complexes of halogens and interhalogen compounds (I_2, Br_2, ICl, and IBr) with certain nitrogen-containing donors are extremely involved and interesting objects for the study of the transferred charge and particularly of its distribution in the acceptor molecule. The NQR spectra of these complexes show that the QIC of the central halogen atoms are greater than the QIC of the same atoms in the individual molecules. To explain this, it has been suggested[39,40] that the acceptor molecules behave as *v* acceptors in the stable complexes of halogens and interhalogen compounds with nitrogen-containing donors. Here the central iodine atom is sp^3d-hybridised, three orbitals are occupied by the lone electron pairs, one is involved in the formation of a covalent bond with another halogen atom, and one is involved in intermolecular interaction.

Table 6. The parameters of the NQR spectra and the degrees of charge transfer in bromine and chlorine complexes.

Complex	ν^*, MHz	b^2, *e*	Complex	ν^*, MHz	b^2, *e*
Br_2	319.54	—	$Cl_2\cdot C_6H_5NO_2$	54.510	
$Br_2\cdot CH_3COCH_3$	318.34	0.01		53.675	0.02
$Br_2\cdot C_6H_5COC_2H_5$	317.18	0.02		53.050	
$Br_2\cdot CH_3COOOCH_3$	318.01	0.02	$Cl_2\cdot C_6H_6$	53.463	0.03
$Br_2\cdot C_4H_8O_2$	314.99	0 04	$Cl_2\cdot C_6H_5CH_3$	53.730	
$Br_2\cdot HCOOC_2H_5$	318.78	0.01		53.595	0.03
$Br_2\cdot 2CH_3OH$	317.95			53.338	
	315.98	0.03		53.128	
$Br_2\cdot C_6H_5Br$	317.85	0.02	$Cl_2\cdot 1,2\text{-}(CH_3)_2C_6H_4$	53.863	
Cl_2	54.247	—		53.530	0.02
$Cl_2\cdot C_4H_8O_2$	53.257	0.04		53.400	
$Cl_2\cdot O(C_2H_5)_2$	53.573	0.02	$Cl_2\cdot 1,4\text{-}(CH_3)_2C_6H_4$	53.533	0.03

* The ^{81}Br and ^{38}Cl wavenumbers respectively are quoted.

The application of the Dailey–Townes theory shows that the degree of charge transfer is in this case 40–50%, which agrees well with infrared spectroscopic and dipole moment data. The authors[41,42] observed only one NQR frequency for the central iodine atom in complexes with nitrogen-containing ligands. Owing to the inadequacy of the experimental data, it was assumed[39] that the amount of ionic character of the iodine–halogen bond does not change on complex formation. On the other hand, the frequencies of the terminal halogen atoms were also observed in the NQR spectra of the complexes $ICl.C_5H_5N$ and $ICl.4\text{-}CH_3C_5H_4N$, [43] as well as the complexes of ICl, IBr, and Br_2 with $3,5\text{-}Br_2C_5H_3N$.[41] The appreciable decrease of these frequencies on complex formation indicates a significant change in the amount of ionic character of the halogen–halogen bonds. Taking this into account, the authors[43,44] estimated the charge distribution in the complexes (Table 7). It was found that there is always a positive charge on the central halogen atom. The study of the NQR spectra[45,46] and calculation by the CNDO method without taking into account the *d* orbitals[47] of the trihalide ions also lead to a positive charge on the central halogen atom. The charge distributions in such ions, calculated by Harada et al.[45] and Gabes et al.[46], are presented in Table 7.

Such charge distribution can be explained within the framework of a three-centre delocalised σ orbital. The simplest wave function of the ground state of stable *nσ* amine–halogen complexes (NX_2) can be formulated as follows:

$$\psi_N = a\psi(N, X_2) + b\psi(N^+—X_2^-).$$

When account is taken of the polarisation of the acceptor molecule, we obtain

$$\psi_N = a\psi(N, X_2) + b_1\psi(N^+XX^-) + c\psi(N^+X^-X) + d\psi(NX^+X^-). \tag{10}$$

The positive charge on the central halogen atom indicates the considerable importance of the polarisation term $d\psi(NX^+X^-)$ in Eqn. (10). In stable *nσ* complexes and trihalide ions, the polarisation of the acceptor molecule apparently plays a significant rôle.

Table 7. The charge distribution in complexes of the *nσ* type and trihalide ions.

Compound	Charge on halogen atom, *e*		Total charge, *e*	Compound	Charge on halogen atom, *e*		Total charge, *e*
	central	terminal			central	terminal	
$(CH_3)_4NI_3$	+0.08	−0.50	−0.92	$CsICl_2$	+0.35	−0.64	−0.93
$(C_2H_5)_4NI_3$	+0.07	−0,50	−0.93	$KICl_2$	+0.28	−0.66	−1.04
$(n\text{-}C_4H_9)_4NI_3$	+0.08	−0.50	−0.92	$(CH_3)_4NIBr_2$	+0.18	−0.58	−0.98
$(n\text{-}C_3H_7)_4NI_3$	+0.05	−0.55	−1.05	$(C_4H_9)_4NIBr_2$	+0.21	−0.60	−0.98
$(CH_3)_2NH_2I_3$	+0.08	−0.51	−0.94	$CsBr_3$	+0.06	−0.52	−0.98
$(n\text{-}C_3H_7)_2NH_2I_3$	+0.08	−0.51	−0.94	$(C_4H_9)_4Br_3$	+0.01	−0.52	−1.04
TlI_3	+0.03	−0.54	−1.06	$Br_2\cdot 3,5\text{-}Br_2C_5H_3N$	+0.10	−0.30	−0.20
CsI_3	+0.08	−0.49	−0.90	$IBr\cdot 3,5\text{-}Br_2C_5H_3N$	+0.30	−0.55	−0.25
NH_3I_3	+0.07	−0.48	−0.88	$ICl\cdot 3,5\text{-}Br_2C_5H_3N$	+0.35	−0.65	−0.30
RbI_3	+0.08	−0.48	−0.89	$ICl\cdot C_5H_5N$	+0.35	−0.61	−0.26

Comparison of the transferred charges calculated using the sp^3d hybridisation of the central atom and three-centre orbitals shows that the degrees of charge transfer in the complexes are similar in the two cases. However, treatment of the problem from different standpoints leads to differences in charge distribution in the acceptors.

The application of the Mössbauer method for the estimation of charge transfer in iodine complexes has been demonstrated[48]. The authors studied the complex $I_2.C_6H_6$. The employment of the dependence of the isomeric shift of ^{127}I on the number of vacancies in the 5*p* shell led to a degree of charge transfer of 26%. This value is not confirmed by data obtained by other methods, including the NQR method[41]. Presumably a relation of this kind does not permit a correct estimate of the degree of charge transfer.

As mentioned previously, a single relation, similar to Eqn. (8), linking the change in the EFG to the degree of charge transfer, cannot be obtained for complexes of *v* acceptors. The formation of complexes by *v* acceptors leads in most cases to a complete rearrangement of the entire electronic system of the molecule and to the formation of one or several additional vacant orbitals. Such rearrangement leads also to a change in the parameters of the metal–halogen bonds (amount of ionic character, amount of double bond character, etc.). In most cases a detailed analysis of the changes in the EFG is therefore possible only on the basis of a detailed calculation for each specific complex. If it is possible to obtain the QIC for all the acceptor atoms, the calculation of charge transfer for a complex with a known geometry can be performed on the basis of the Dailey–Townes theory. Otherwise, one can only consider qualitative changes in the degree of charge transfer within the limits of a series of complexes.

Interesting results have now been obtained for complexes of Group III, IV, and V metal halides. Much attention has been devoted[49–52] to the study of the octahedral complexes $SbCl_5.L$. The known geometry of the complexes[51] made it possible to carry out calculations by the molecular orbital method. It was shown that the electron density at the equatorial chlorine atoms should be smaller than at the axial atom. Indeed, such electron density distribution has been observed in the complexes of $SbCl_5$ with methyl and ethyl alcohols, acetonitrile, and dimethylformamide. On the other hand, in the remaining complexes the steric influence of the donor molecules on the quadrupole frequencies of the equatorial chlorine atoms is pronounced and the NQR frequencies of chlorine cannot be assigned to the axial and equatorial atoms. However, the employment of average frequency shifts on complex formation makes it possible to estimate the degree of charge transfer Δ and the charge distribution in all $SbCl_5.L$ complexes. Table 8 presents data for all the $SbCl_5.L$ complexes investigated[51,52] with $e^2Qq^{Sb}_{am}$ = 1300 MHz [53] and a positive sign of the EFG at the antimony atom[54,55]; Δ_{Sb} is the change of the charge of the antimony atom on complex formation and Δ_{Cl} the corresponding change for all the chlorine atoms. Table 8 shows that complex formation results in a significant increase of electron density at the chlorine atoms of the acceptor molecule and in a slight decrease of the electron density at the antimony atom.

Table 8. The degrees of charge transfer in the complexes $SbCl_5.L$.

Complex	Δ, e	Δ_{Sb}, e	Δ_{Cl}, e	Complex	Δ, e	Δ_{Sb}, e	Δ_{Cl}, e
$SbCl_5 \cdot POCl_3$	0.26	—0.04	0.30	$SbCl_5 \cdot CH_3OH$	0.29	—0.11	0.40
$SbCl_5 \cdot CH_3CN$	0.23	—0.09	0.32	$SbCl_5 \cdot C_2H_5OH$	0.28	—0.11	0.39
$SbCl_5 \cdot C_6H_5CN$	0.24	—0.09	0.33	$SbCl_5 \cdot (CH_2Cl)_2O$	0.25	+0.02	0.23
$SbCl_5 \cdot ClCN$	0.20	—0.12	0.32	$SbCl_5 \cdot (CH_2)_4O_2$	0.28	—0.11	0.39

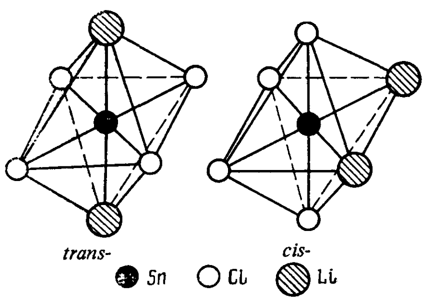

Figure 1. The *cis–trans* isomerism in the octahedral complexes $SnCl_4.L_2$.

Among the complexes of Group IV elements, very vigorous studies are being made on the octahedral complexes $SnCl_4.L_2$ (Fig. 1) both by the NQR method[42,56–59] and by Mössbauer spectroscopy[60–63]. One should note that, whereas the degree of charge transfer in the complexes $SbCl_5.L$ was estimated from the known QIC of the antimony atom obtained from the NQR spectra, in the complexes $SnCl_4.L_2$ the degree of charge transfer was calculated using the quadrupole splitting by the tin atom observed in the Mössbauer spectra[64,65]. Table 9 presents the calculation of the degree of charge transfer in all the $SnCl_4.L_2$ complexes investigated hitherto, taking into account the sign of the EFG at the tin atom[60]. As in the complexes $SbCl_5.L$, there is a significant increase of electron density at the chlorine atom in the acceptor. However, in contrast to the complexes $SbCl_5.L$, there is a fairly considerable increase of the positive charge of the tin atoms in almost all the complexes $SnCl_4.L_2$. It is also important to note[64] (Table 10) that, as expected from calculations by the molecular orbital method[56], in complexes having a *cis*-structure, the electron density at the axial chlorine atoms is smaller than at the equatorial atoms. Such redistribution of electron density is consistent with the concept of the mutual influence of ligands in complexes of non-transition elements[66].

Table 9. The degrees of charge transfer in the complexes $SnCl_4.L_2$.

Complex	Δ, e	Δ_{Sn}, e	Δ_{Cl}, e
$SnCl_4 \cdot 2CH_3OH$	0.37	—0.08	0.45
$SnCl_4 \cdot 2C_2H_5OH$	0.39	—0.05	0.44
$SnCl_4 \cdot 2(CH_2)_4O_2$	0.27	—0.13	0.40
$SnCl_4 \cdot 2(CH_2)_4O$	0.23	—0.21	0.44
$SnCl_4 \cdot 2(C_2H_5)_2O$	0.27	—0.13	0.40
$SnCl_4 \cdot 2CH_3CN$	0.34	0	0.34
$SnCl_4 \cdot 2C_6H_5CN$	0.40	0	0.40
$SnCl_4 \cdot 2HCON(CH_3)_2$	0.35	—0.21	0.56
$SnCl_4 \cdot 2(CH_3)_2SO$	0.46	—0.05	0.51
$SnCl_4 \cdot 2[3\text{-}CH_3C_5H_4N]$	0.38	—0.18	0.56
$SnCl_4 \cdot 2(i\text{-}C_3H_7)_2PO(SCH_3)$	0.34	—0.18	0.52
$SnCl_4 \cdot 2(i\text{-}C_3H_7O)_2PO(SCH_3)$	0.23	—0.24	0.47

Table 10. The charge distribution in the *cis*-complexes $SnCl_4.L_2$.

Complex	Δ^{ax}_{Cl}, e	Δ^{eq}_{Cl}, e	Δ_{Cl}, e
$SnCl_4 \cdot 2CH_3OH$	0.17	0.28	0 45
$SnCl_4 \cdot 2C_2H_5OH$	0.16	0.28	0.44
$SnCl_4 \cdot 2(CH_3)_2CO$	0.17	0.23	0.40
$SnCl_4 \cdot 2CH_3CN$	0.15	0.19	0.34
$SnCl_4 \cdot 2POCl_3$	0.14	0.20	0.34
$SnCl_4 \cdot 2CH_3OCH_2Cl$	0.10	0.18	0.28
$SnCl_4 \cdot 2(CH_3)_2SO$	0.24	0.27	0.51

Calculation for the complex of $SnBr_4$ with hexamethylphosphoramide from the data of Petrosyan et al.[67] and Philip et al.[68] yielded a transferred charge of 0.37 e. The nature of the change in the charge on the acceptor atoms proved to be the same as in the complexes $SnCl_4.L_2$. The negative charge on the bromine atoms increases by 0.60 e while the positive charge on the tin atom increases by 0.23 e.

The study of the complexes $SbCl_5.L$ and $SnCl_4.L_2$ using the Mössbauer effect[54,55,60–63] should yield information about the populations of the 5s and 5p orbitals of the antimony and tin atoms. Fig. 2 presents the relation between the isomeric shift δ and the QIC of ^{121}Sb in certain complexes $SbCl_5$. RCN.[54] An increase of the isomeric shift leads to an increase of the QIC. The parallel variation of δ and QIC for ^{119m}Sn is also observed for the complexes $SnCl_4.L_2$. The relation may be caused both by a decrease of the population of the 5*s* orbitals by an increase of the shielding of the 5*p* orbitals[69]. It is therefore impossible to discover unambiguously for both types of complexes, on the basis of the Mössbauer spectra, how the populations of the orbitals of the antimony and tin atoms change on complex formation.

Among complexes of Group III elements, Tong made a detailed study of the complexes of $GaCl_3$ with a number of *n* donors[70]. The lack of specific data for NQR frequencies precludes the calculation of the degrees of charge transfer in these complexes. However, the relation between the ^{35}Cl and ^{69}Ga NQR frequencies permitted the estimation of the charge distribution in these complexes. It has been shown[39] that 2/7 of the transferred charge is located at the gallium atom and 5/7 is distributed between the three chlorine atoms.

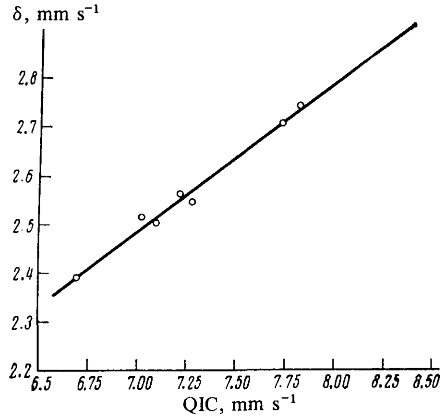

Figure 2. Relation between δ and the ^{121}Sb QIC in the complexes $SbCl_5.RCN$.

The complexes of antimony and arsenic trihalides with aromatic bases have been very widely investigated[71-75]. The attempt to estimate the degrees of charge transfer in these complexes undertaken by the present authors[75] was unsuccessful owing to the incorrect selection of the sign of the EFG at the nucleus of the antimony atom[76, 77]. This failure is probably associated with the lack of the exact knowledge of the hybridisation of the antimony and arsenic atoms in these complexes.

A Mössbauer study of the complexes $n SbHal_3.Ar$ [76, 77] yielded additional information about charge transfer in them. The authors believe that the population of the 5*s* orbitals of the antimony atom varies insignificantly owing to the slight change of the isomeric shift. The use of the relation between the isomeric shift and the population of the 5*p* orbitals of the antimony atom[78] made it possible to estimate the latter[76] (Table 11). However, as shown previously, the decrease of the isomeric shift is caused both by the decrease of the population of the 5*s* orbitals of antimony and by the increase of the shielding of the 5*p* orbitals[69]. The results presented in Table 11 are therefore to some extent controversial.

A study was made of the change in the charge on the acceptor atoms in all the complexes. There is no doubt that the changes in the charge on the donor atoms are of considerable interest. Unfortunately, there have been virtually no NQR studies on these lines. Only two investigations may be noted. Negita et al.[79] studied the complexes of acetonitrile with chlorine and bromine. The observation of NQR signals due to the nitrogen and halogen nuclei made it possible to estimate the degree of charge transfer in these complexes both from the NQR spectrum of the donor and from the spectrum of the acceptor (Table 12). The authors' explanation of the difference between the transferred charges calculated from the ^{14}N and ^{81}Br QIC is that part of the charge is transferred from the CH_3CN molecule via the d_z^2 orbitals of the bromine atom, which make a much smaller contribution to the EFG than the p_z orbitals.

Table 11. The degrees of charge transfer in the complexes $n SbCl_3.Ar$ from Mössbauer spectroscopic data[76]*.

Complex	n_p	Δ, *e*	$\vert\psi(0)\vert^2/a_0^3$
$SbCl_3$	1.35	—	33.0
$2SbCl_3 \cdot C_6H_6$	1.57	0.22	32.5
$2SbCl_3 \cdot C_6H_5CH_3$	1.47	0.12	32.9
$2SbCl_3 \cdot 1,4\text{-}(CH_3)_2C_6H_4$	1.53	0.18	32.6
$SbCl_3 \cdot 1,3,5\text{-}(CH_3)_3C_6H_3$	1.60	0.25	32.3
$2SbCl_3 \cdot C_6H_5OCH_3$	1.53	0.18	32.6
$SbCl_3 \cdot C_6H_5C_2H_5$	1.30	—	33.1
$2SbCl_3 \cdot C_6H_5C_6H_5$	1.35	—	33.0
$2SbCl_3 \cdot C_{10}H_8$	1.50	0.15	32.8

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*n_p is the number of vacancies in the 5*p* shell of the antimony atom, Δ the degree of charge transfer, and $|\psi(0)|^2/a_0^3$ the overall electron density of the antimony nucleus.

Table 12. The degrees of charge transfer in the complexes $2CH_3CN.Hal_2$.

Complex	Change in charge, *e*	
	on nitrogen	on halogen
$2CH_3CN \cdot Cl_2$	+0.028	−0.021
$2CH_3CN \cdot Br_2$	+0.029	−0.00

The charge distribution in the complexes $AlBr_3.SbBr_3$ and $AlBr_3.BiBr_3$ has been investigated[80]. The transferred charge Δ was calculated from the QIC of the antimony, bismuth, and bromine atoms forming part of the donor molecules. The change in the charge on the aluminium atom in consequence of complex formation was estimated relative to the Al_2Br_6 dimer from the change in the QIC of the bromine atoms. The results (Table 13) showed that the charge in the donor molecules is transferred directly from the lone pair of the central atom and hardly involves the halogen atoms of the donor.

Thus the application of the NQR and Mössbauer methods to the calculation of the degree of charge transfer and of charge distribution in the complexes leads to very interesting results. The degree of charge transfer is satisfactorily correlated with data obtained by other methods. The most important factor is that NQR and the Mössbauer effect made it possible to obtain the distribution of the transferred charge, in contrast to the other methods described previously. One can now assume that both in complexes of the $n\sigma$ type and in complexes of v acceptors, the polarisation of the valence shells of the central complex-forming atom apparently plays a significant role. Furthermore, in v-acceptor molecules, the changes in atomic charges on complex formation are associated with the changes in the hybridisation of the central atom.

Table 13. The degrees of charge transfer in the complexes $AlBr_3.L$.

Complex	Δ, e	$\Delta_{Sb\,(Bi)}$, e	Δ'_{Br}, e	Δ_{Al}, e	Δ_{Br}, e
$AlBr_3 \cdot SbBr'_3$	0.20	—0.15	—0.05	—0.08	0.28
$AlBr_3 \cdot BiBr'_3$	0.27	—0.29	0.02	—0.05	0.32

VI. X-RAY ELECTRONIC SPECTROSCOPY

X-Ray electronic spectroscopy of complexes has been developing very vigorously recently. The application of X-ray electronic spectra in the study of donor–acceptor interaction is based on the parallel variation of the effective charges of the atoms investigated and of the shift of the X-ray electronic lines. One can therefore infer the changes in the electron densities at the atoms from the changes in the energy of the binding of electrons (E_b).

Using the electrostatic potential model[81], the shift of the internal energy level can be formulated thus:

$$\Delta E_b = Kq_i + V_i + l, \tag{11}$$

where

$$V_i = \sum_{j \neq i} q_j / R_{ij}$$

is the molecular potential in the vicinity of the nucleus i, q_i the charge on the atom i, R_{ij} the distance between the nuclei i and j, and l a constant determined by selecting the starting point of the readings. The constant K is approximately equal to the integral of the electrostatic interaction between the internal orbital under consideration and the valence orbital in the same atom. Eqn. (11) can be simplified to

$$\Delta E_b = K'q_i.$$

According to the free ion model[82], $K' \simeq 1/r$, where r is the radius of the valence shell. The radius of the radial distribution density of valence electrons in carbon, oxygen, and nitrogen atoms is approximately 1 Å (1 Å $\simeq$ 2 atomic units) and, when a single electron is removed, the shift in the binding energy of the internal electrons per unit charge is 14 eV.

The free ion model can be improved by taking into account the fact that the valence electrons are not transferred to an infinite distance on formation of a chemical bond. If the distance between the nuclei is R_{ij}, the shift of the internal electron energy can be formulated as follows:

$$\Delta E_b = \left(\frac{1}{r} - \frac{\alpha}{R_{ij}}\right) q_i, \tag{12}$$

where α is the Madelung constant[83]. For ionic crystals, the shift of the internal electron energy calculated by Eqn. (12) is approximately 5 eV per unit charge. However, it is clear that the use of even an improved free ion model for the calculation of the shift of the internal electron energy when one electron is removed in complexes with appreciably covalent bonds cannot in principle lead to a satisfactory quantitative estimate of the degree of charge transfer. This is why the degree of charge transfer which we estimated with the aid of the improved free ion model does not agree very well with data obtained by other methods.

Charge transfer in the complex $ICl.C_5H_5N$ has been investigated[84] using K' = 14 eV per unit charge. A change in the energy of the ^1S state of the nitrogen atom by 0.9 eV leads to the appearance of a +0.06 e charge on the nitrogen atom of the pyridine molecule. When we used K' = 5 eV per unit charge, the charge on the nitrogen atom was found to be +0.18 e, i.e. closer to the transferred charge obtained from dipole moment and NQR data.

The photoelectronic spectra of certain complexes of tin halides have been studied[85] and the shift of the internal electrons of the donor atom directly involved in complex formation has been determined[85]. We estimated the degree of charge transfer Δ in these complexes also using K' = 5 eV per unit charge (Table 14).

Table 14. The degrees of charge transfer in the complexes $SnCl_4.L_2$ obtained from photoelectronic spectra[92].

Complex	ΔE_b, eV	Δ, e
$SnBr_4 \cdot 2(C_6H_5)_3PO$	0.2	0.04
$SnCl_4 \cdot 2(C_6H_5)_3PO$	0.2	0.04
$SnCl_4 \cdot 2(CH_3)_2NCS$	0.9	0.18
$SnBr_4 \cdot \alpha, \alpha'\text{-}C_{10}H_8N_2$	1.7	0.34
$SnCl_4 \cdot 2C_5H_5N$	2.0	0.40

A recently published report[86] describes a study of photoelectronic spectra of $SbCl_5$ solutions for certain n-donor solvents. The energies of the binding of $3d_{5/2}$ internal electrons of the antimony atom were compared with the enthalpies of formation of the complexes or with Gutman's donor numbers (DN).[87] The observed correlation between ΔE and DN (Fig. 3) is described by a straight line. However, it is known that the change in electron density at halogen atoms in the complexes obtained from NQR spectra (Δ_{Cl}) depends directly on DN.[67] Comparison of these two correlations, the dependence of ΔE on DN and of Δ_{Cl} on DN, makes it possible to obtain the relation between ΔE and Δ_{Cl}, which can be represented in the following form:

$$\Delta E = 321.5 + 3.16 \Delta_{Cl} \pm 0.2 \text{ (eV)}. \tag{13}$$

The fairly large error precludes quantitative estimates of the shift of the binding energy of the internal electrons of the antimony atom, but Eqn. (13) permits a qualitative estimate of the change in this energy.

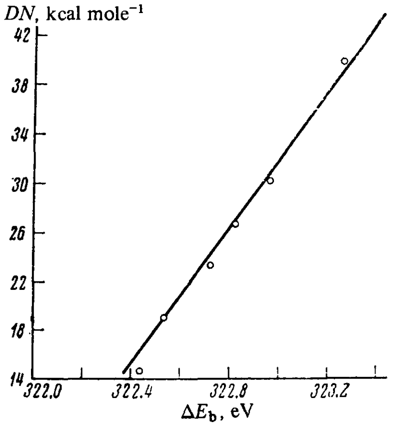

Figure 3. Relation between ΔE_b and DN.

It is now clear that X-ray electronic spectroscopy together with NQR and quantum-chemical calculations can yield unique information about the charge distribution in complexes among all the atoms of the interacting molecules. However, there have been so far no studies dealing with the X-ray electronic spectra of all the atoms in the complex. It is therefore of interest to carry out such investigations with the aid of the X-ray electronic spectra of the complexes which have been studied by other methods.

VII. QUANTUM-CHEMICAL CALCULATIONS

Quantum-chemical calculations constitute nowadays one of the principal methods whereby one can estimate the changes in the charge on each atom of the complex. However, the charge depends markedly on the chosen method of calculation. The most rigorous calculations of the *ab initio* type can be carried out only for small molecules with a small number of orbitals. On the other hand, semi-empirical calculations yield an electron density distribution which depends significantly on the choice of the parameters of the calculation. Furthermore, the use of semi-empirical methods for calculations on complexes is limited by the lack of sufficiently reliable parameters for elements with a large number of orbitals. As a result, comparatively few calculations have so far been made on complexes of the $\pi\sigma$, $n\sigma$, and nv types.

We shall begin the discussion of the available data with non-empirical methods, which lead to more accurate results.

A calculation has been made[88] on BF_3 complexes with various ligands by the *ab initio* method. Table 15 presents the distributions of the transferred charge in the acceptor molecule which were calculated from the orbital populations. It can be readily seen that there is a significant shift of electron density in these complexes to the fluorine atoms ($\Sigma\Delta_F$) of the acceptor molecule. Furthermore, part of the charge is transferred to the boron atom (Δ_B). The distribution of the transferred charge in the acceptor molecule is different for different complexes. Table 15 presents the ratios of the charge transferred to the boron atom and of the degree of charge transfer (Δ_B/Δ).

Table 15. The degrees of charge transfer in the complexes $BF_3.L$.[88]

L	Δ, e	Δ_B, e	Δ_F, e	$\Sigma\Delta_F$, e	Δ_B/Δ, e
NH_3 (eclipsed)	0.269 0.269	0.092 0.080	0.059 0.063	0.177 0.189	0.34 0.30
NH_3 (staggered)	0.285 0.285	0.105 0.093	0.060 0.064	0.180 0.192	0.37 0.33
H_2O	0.217 0.217	0.052 0.040	0.055 0.059	0.165 0.177	0.24 0.18
H_2S	0.297 0.297	0.204 0.192	0.031 0.035	0.093 0.105	0.69 0.65
Ne	0.122 0.122	0.047 0.035	0.025 0.029	0.075 0.087	0.39 0.29
Ar	0.215 0.215	0.146 0.134	0.023 0.027	0.069 0.081	0.68 0.62
CO	0.074 0.074	−0.010 −0.022	0.028 0.032	0.084 0.096	−0.14 −0.30
F^-	0.411 0.411	0.090 0.078	0.107 0.111	0.321 0.333	0.22 0.19
Cl^-	0.472 0.472	0.250 0.238	0.074 0.078	0.222 0.234	0.53 0.50

Much attention has been devoted to calculations on borazane BH_3NH_3.[89-95] The results of these studies agree well with one another. As an example, Table 16 lists the populations of the atomic orbitals in the BH_3, NH_3, and $BH_3.NH_3$ molecules[89] and our calculated degrees of charge transfer Δ. The greatest changes were observed in the populations of the $2p_z$ orbitals of the boron and nitrogen atoms. When the complexes are formed, 0.1 e is transferred to the orbitals of the boron atom and 0.16 e to the 1s orbitals of the three hydrogen atoms. Evidently, in this complex there is also a significant displacement of electron density to the hydrogen atoms of the acceptor molecule. The complexes $BH_3.CO$,[89] $BF_3.C_6H_5CHO$,[96] BF_3 complexes with ethers[97], and $BH_3.PH_3$[98] have also been investigated by the *ab initio* method. All the calculations lead to the same charge distributions as for the complex $BH_3.NH_3$. One need only note that, in the boron halide complexes, the shift of electron density to the halogen atoms is greater than the shift to the hydrogen atoms in the BH_3 complexes. This is probably associated with the greater electronegativity of the halogen atoms.

We can now proceed to the discussion of the semi-empirical methods for calculations on complexes. Calculations have been made[99,100] on complexes of iodine with benzene, pyrrole, furan, and thiophen on the basis of the perturbation theory. The change in charge distribution in the $I_2.C_6H_6$ complex[99] is illustrated in Fig. 4, which shows that the charge is distributed uniformly between the two iodine atoms. In the remaining complexes, the charge distribution is similar. However, the use of more accurate methods of calculation leads to a different charge distribution in the acceptor molecule. Thus the electronic structures of the complexes $I_2.C_6H_6$ and $I_2.NH_3$ have been investigated[101] by a modified PNDO method. An excess positive charge of 0.06 *e* appears in the $I_2.C_6H_6$ complex on the iodine atom directly coordinated to the ring, while on the other iodine atom there is a negative charge of −0.09 *e*. Such charge distribution is consistent with the marked influence of polarisation in the complexes. The charge distribution in the complex $I_2.NH_3$ (Fig. 5*a*) is the same as in the benzene complex, but the low degree of charge transfer is inconsistent with experimental data for iodine complexes with *n* donors. The charge distribution in the complexes $F_2.NH_3$ and $Cl_2.NH_3$, obtained by the PNDO method[102], is illustrated in Figs. 5*b* and 5*c*. The electron density at the halogen atoms linked directly to the nitrogen atom is also reduced in these complexes.

Table 16. The orbital populations in $BF_3.NH_3$.[89]

Atom	Orbital	BH_3	NH_3	$BH_3 \cdot NH_3$	Δ, *e*
B	s	3.137		2.994	−0.143
	$2p_x$, $2p_y$	0.902		0.876	−0.026
	$2p_z$	0		0.275	0.275
H_B	s	1.020		1.075	0.055
N	s		3.516	3.518	0.002
	$2p_x$, $2p_y$		1.210	1.347	0.137
	$2p_z$		1.861	1.677	−0.184
H_N	s		0.734	0.621	−0.113

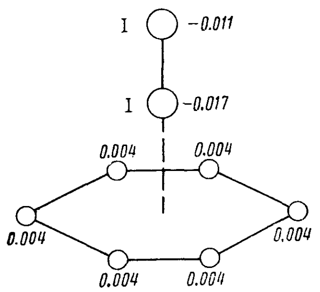

Figure 4. The changes in the atomic charges in the complex $I_2.C_6H_6$.[97] The charges are positive on the I atoms and negative on the C atoms.

Among complexes of *v* acceptors, the calculation on the octahedral complex $TiCl_4.2HCN$ by the CNDO method[103] is of interest. The calculation is one of the first designed to investigate the electronic structure of complexes of the donor–acceptor type in which the central atom contains *d* electrons. The calculated degree of charge transfer proved to be 0.2 *e*. It is interesting to trace the changes in the populations of the valence atomic orbitals on complex formation. Table 17 shows that the population of the *s* orbitals of the titanium atom diminishes, the overall population of the *p* orbitals increases, and the population of the *d* orbitals remains unchanged. There is a significant increase in the pupulations of the p_z and d_{z^2} orbitals of the titanium atom on complex formation, but, owing to the decrease of the populations of the other orbitals, the overall charge on the titanium atom remains unchanged. There is a significant increase in electron density at the chlorine atoms, the increase being greater at the equatorial atoms than at the axial atoms. Although the titanium atom has a partially filled *d* shell, in contrast to tin or antimony atoms, the similarity of the complex formation processes permits a comparison of the charge distribution in the acceptor molecule in the $TiCl_4.L_2$ complexes with that in the complexes $SbCl_5.L$ and $SnCl_4.L_2$. Table 17 shows that the nature of the changes in the charge on the acceptor atoms in the $TiCl_4.L_2$ complexes is the same as in the complexes $SbCl_5.L$ and $SnCl_4.L_2$, which has been demonstrated by the NQR method.

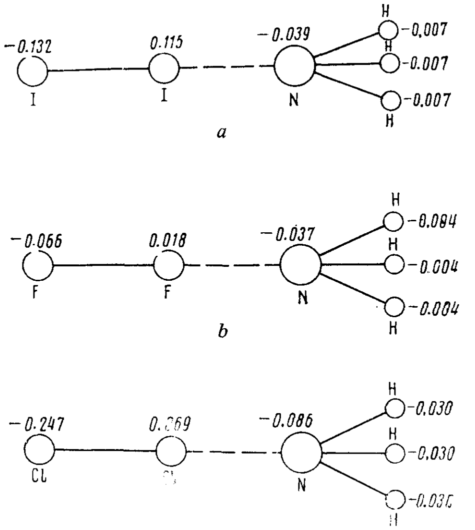

Figure 5. The changes in the atomic charges in the complexes $NH_3.Hal_2$.[99,100] The charges are positive on the halogen atoms remote from the nitrogen atoms and negative on the halogen atoms linked to the nitrogen atoms.

Table 17. The orbital populations in the complex $TiCl_4.2HCN$.[103]

Atom	Orbital	$TiCl_4$	HCN	$TiCl_4 \cdot 2HCN$	Atom	Orbital	$TiCl_4$	HCN	$TiCl_4 \cdot 2HCN$
Ti	s	0.31	—	0.21	N	s		1.80	1.75
	p_x	0.15		0.16		p_x		1.16	1.20
	p_y	0.15		0.14		p_y		1.16	1.19
	p_z	0.15		0.26		p_z		1.06	1.03
	$d_{x^2-y^2}$	0.17		0.12		q		−0.18	−0.22
	d_{xy}	0.44		0.53	C	s		1.49	1.16
	d_{z^2}	0.17		0.69		p_x		0.87	0.85
	d_{yz}	0.44		0.14		p_y		0.88	0.85
	d_{xz}	0.44		0.19		p_z		0.95	0.93
	q	1.56		1.56		q		0.11	0.21
$Cl^{ax}_{1,2}$	s	1.97		1.99	H	s		0.93	0.89
	p	5.42		5.44		q		0.07	0.11
	q	−0.39		−0.43					
$Cl^{eq}_{3,4}$	s	1.97		1.99					
	p	5.42		5.46					
	q	−0.39		−0.45					

Calculations have been made[104] on complexes of organometallic compounds and boron and aluminium halides by the CNDO method. Table 18 presents the changes in the charges of the component atoms which we calculated from the authors' data. As in the preceding calculations, the formation of boron and aluminium halide complexes entails a significant increase of electron density at the halogen atoms.

Calculations have been made by the Hückel method for a number of BF_3 complexes[105-107], where the charge distribution in the acceptor molecule proved to be similar to the charge distribution obtained in calculations by more accurate methods.

One must note that, although different methods of calculation yield different orbital populations, the transferred charge and the nature of its distribution in the same complexes depend little on the specific method of calculation. The charge distribution obtained by quantum-chemical calculations on complexes of both σ and v acceptors agree well with the charge distribution obtained with the aid of experimental methods for the investigation of complex compounds.

Table 18. The degrees of charge transfer in boron and aluminium complexes.

Complex	Δ, *e*	$\Delta_{B(Al)}$, *e*	$\Sigma\Delta_{CH_3(Cl)}$, *e*	Δ_N, *e*	$\Sigma\Delta_{CH_3}'$, *e*	$\Delta_{B(Al)}/\Delta$, *e*
$B(CH_3)_3 \cdot N(CH_3)_3$	0.41	0.12	0.30	—0.16	—0.24	0.30
$BCl_3 \cdot N(CH_3)_3$	0.57	0.03	0.54	—0.19	—0.36	0.05
$Al(CH_3)_3 \cdot N(CH_3)_3$	0.38	0.22	0.16	—0.12	—0.24	0.60
$AlH_3 \cdot N(CH_3)_3$	0.42	0.41	0.02	—0.11	—0.30	0.98
$AlCl_3 \cdot N(CH_3)_3$	0.46	0.18	0.29	—0.14	—0.30	0.40

Table 19. Comparison of the degrees of charge transfer obtained by different methods.

Complex	i.r. Spectra	μ_{DA} (Δ H)	NQR	Quantum-chemical calculations
$Cl_2 \cdot C_6H_6$	0.06	—	0.03	—
$Br_2 \cdot 2CH_3CN$	0.06	—	0.03	—
$I_2 \cdot C_6H_6$	0.07	0.03 0.08	0.08	0.03
$I_2 \cdot NH_3$	—	0.13	—	0.04
$I_2 \cdot C_5C_5N$	0.21	0 23	0.21	—
$I_2 \cdot (CH_3)_3N$	0.43	0.34	—	—
$I_2 \cdot (CH_3)_2S$	0.30	0.22	—	—
$ICl \cdot C_5H_5N$	0.46	—	0.26	—
$ICl \cdot 4\text{-}CH_3C_5H_4N$	0.46	—	0.26	—
$IBr \cdot CH_3CN$	0.12	0.12	—	—
$BF_3 \cdot C_5H_5N$	—	0.71	—	0.48
$BCl_3 \cdot (CH_3)_3N$	—	0.86	—	0.57
$B(CH_3)_3 \cdot N(CH_3)_3$	—	0.50	—	0.41
$Al(CH_3)_3 \cdot N(CH_3)_3$	—	0.85	—	0.38
$SnCl_4 \cdot 2C_4H_8O$	—	0.68	0.23	—
$SnCl_4 \cdot 2CH_3CN$	—	0.34	0.34	—
$SnCl_4 \cdot 2C_6H_5CN$	—	0.29	0.40	—
$SbBr_3 \cdot AlBr_3$	—	0.23	0.20	—
$SbCl_5 \cdot CH_3OH$	—	0.54	0.29	—
$SbCl_5 \cdot CH_3CN$	—	0.40	0.23	—
$SbCl_5 \cdot POCl_3$	—	0.33	0.26	—

VIII. CONCLUSION

All the methods which have been used to determine the degree of charge transfer can be divided into two groups. One group includes the dipole moment and infrared spectroscopic methods. The degree of charge transfer is determined either from the dipole moment of the donor–acceptor bond or with the aid of force constants (or the stretching vibration frequencies) of the bonds. The nature of the changes in the charge on the atoms in the donor and acceptor molecules cannot then be determined. This is because the experimental quantities refer solely to the bonds and do not therefore permit inferences about the changes in the atomic charges. The second group of methods includes NQR, Mössbauer spectroscopy, X-ray electronic spectroscopy, and quantum-chemical calculations, which characterise directly the atoms in the molecule, and therefore permit estimates of the effective atomic charges.

Comparison of the degrees of charge transfer calculated for the same complexes by different methods permit certain conclusions. Although the methods in the second group, with the exception of quantum-chemical calculations, do not take into account the electron density in the region of the overlap of the wave functions of the donor and the acceptor, the numerical values of the degree of charge transfer are similar (Table 19). This shows that the electron density in the region of the donor–acceptor bond does not contribute significantly to the degree of charge transfer.

It is so far difficult to assess the accuracy of the charge transfer data obtained and it is therefore impossible to decide which method leads to more correct results. This is because each method is associated with certain assumptions, the role of which is not always susceptible to exact experimental estimation. Furthermore, one must bear in mind that neither the possibility of the formation of a π bond between the donor and acceptor molecules nor the possibility of their mutual polarisation is as a rule taken into account in calculations on the degree of charge transfer. In general, one should note that a procedure whereby account can be taken of polarisation in the estimation of the degree of charge transfer in stable complexes has been hardly developed so far, although it has been shown above that polarisation may play a significant role in complex formation processes.

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Mass-spectrometric Analysis of Solids Using Laser Ion Sources

G.A.Maksimov and N.V.Larin

The development of lasers has permitted their application in the evaporation and ionisation of comparatively small sections of the solids to be investigated with subsequent mass-spectrometric analysis of the vapours and ions formed. Mass-spectrometric analysis using lasers has many advantages compared with the traditional procedures (spark, thermal emission) for the ionisation of solids. In the review, attention is concentrated on the analytical characteristics of the method of the laser evaporation and ionisation of solids in the ion sources of mass-spectrometers.
The bibliography includes 61 references.

CONTENTS

I. INTRODUCTION

The development of radioelectronics, the physics of superconductors, nuclear energetics, and other fields of science and engineering has led to a need for methods of analysis of high-purity solids. The optical, emission, radioactivation, and X-ray fluorescence analytical methods were developed first, and followed in recent years by mass-spectrometric analysis using a spark ion source[1].

The development of laser techniques [2,3] permitted the application of lasers in the evaporation and ionisation of comparatively small sections of test solids with subsequent mass-spectrometric analysis of the ions formed. Mass-spectrometric analysis employing lasers has many advantages, which include the comparatively simple design of the mass-spectrometer having a laser ion source, rapidity of analysis, the possibility of layer-by-layer studies and local analysis of the surface of solids, the simplicity of the mass spectra obtained, and the possibility of analysing not only metals and semiconductors, but also dielectrics. All these factors make mass spectrometry with a laser ion source very promising for the investigation of the content and distribution of impurities in solids. In the first studies on the interaction of laser radiation with solids, use was made of mass spectrometers of the Mattauch–Herzog type[4] as well as time-of-flight instruments [5,6].

Two fundamental operating modes of pulsed lasers are distinguished: the free running mode and the use of a Q-switched resonator[2] ("giant" pulses). In the first case, the radiation pulse has a lifetime $\tau \simeq 10^{-3}$–10^{-4} s and a power $P \simeq 10^3$–10^6 W. For giant radiation pulses, $\tau \simeq 10^{-7}$–10^{-9} s and $P \simeq 10^6$–10^8 W. The interaction of the laser radiation pulse with the substance depends significantly [2,3] on the time τ and P. In this review, we shall therefore consider separately the application in mass-spectrometric analysis of lasers operating in different modes. Attention will be concentrated on the analytical characteristics of the method of laser evaporation and ionisation of solids in the ion sources of mass-spectrometers.

II. ANALYSIS USING A LASER OPERATING UNDER FREE RUNNING CONDITIONS

Under the influence of the laser pulse with a lifetime $\tau \simeq 10^{-3}$ s and a power density of the focussed radiation $q \simeq 10^5$–10^7 W cm^{-2}, a given section of the test specimen undergoes intense evaporation. The diameter of the resulting crater is determined by the conditions of focussing of the radiation and its depth[3] can vary from 10 μm to 10^3 μm, depending on the type of substance, the duration of the pulse, and the energy density in the beam.

The vapour of the substance formed in the laser flash is partly ionised. The ratio of the neutral and ionised vapour components is described satisfactorily by the Sacha–Langmuir equation[4]. The neutral vapour component has a kinetic energy spread $\Delta T \simeq 1$ eV and, after its ionisation (for example by an electron beam), can be analysed with respect to mass in a time-of-flight mass-spectrometer with single space-time focussing. The ionic component of the vapour [2,3] is characterised by the quantity $\Delta T \leqslant 10$ eV. In order to achieve adequate mass resolution, one therefore employs a double focussing instrument or a time-of-flight instrument in which the ionic component is accelerated to energies T such that $\Delta T/T \ll 1$ (the condition for a monoenergetic ion beam).

The problems of the mass-spectrometric applications of lasers operating in the free running mode for the determination of the composition of solids and the investigation of the distribution of impurities in the specimens have been discussed in a number of cases[7-29]. A large group of investigations[7-13,18] have been devoted to the analysis of gases in solids. A typical experimental arrangement[7-9] is illustrated in Fig. 1. The gas evolved from the specimen under the influence of the radiation enters the ion source of a MSKh-3 Chronotron (or MSKh-3A) time-of-flight instrument, where it is partly ionised by the electron beam and, after passing through the drift tube, is recorded by the electron multiplier. In order to eliminate the single-pulse nature of the recording of the spectra and accumulate the evolved gases, the effusion method[17] has been used[13].

A number of investigators[10-12,18] placed the test specimen between the electrodes of the ion source of the MSKh-3A instrument to improve the sensitivity of the analysis. The working pressure in the measuring chamber of the mass-spectrometer was maintained at a level of 5×10^{-9}–5×10^{-8} mmHg and the mass resolution did not exceed 20.

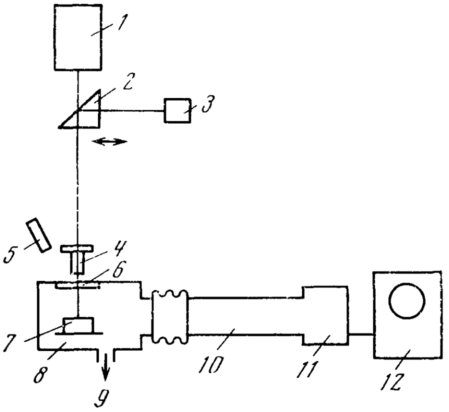

Figure 1. Schematic representation of the instrument with a time-of-flight analyser: 1) laser; 2) prism; 3) eye-piece; 4) object lens; 5) illuminator; 6) inlet window; 7) specimen; 8) vacuum chamber; 9) outlet to vacuum point; 10) "Chronotron" sensor; 11) electronic component; 12) secondary electron multiplier.

By applying the method of calibration graphs, procedures were developed for the quantitative analysis of hydrogen, oxygen, and nitrogen, in titanium, silicon, and zirconium specimens[8,9] as well as in aluminium, titanium, and niobium alloys[11,12]. Reference specimens would apparently extend the range of substances susceptible to analysis by the above method. The experiments carried out with silicon of different origins[8] yielded identical dimensions of the craters formed by the laser pulse regardless of the impurity concentration. Consequently the volume of the sample taken for analysis is independent of the content of the alloying impurities, which leads to a linear relation between the height of the mass-spectrometric peak for the impurity and its concentration in the specimen. Over a wide range of impurity concentrations, the calibration graph consists of a straight line with a slope determined by the type of impurity and the matrix in which it is contained.

In estimating the sensitivity of the method, investigators[9,11,12] used specimens saturated by the given gas to a specified concentration. The lower limit of the observation was[12] 1×10^{-4} wt.% for oxygen and nitrogen, and 5×10^{-5} wt.% for hydrogen with 95% confidence limits. A decrease of the pressure of the residual gases by evacuating the system led to a further improvement of sensitivity[9].

It was shown that the degree of localisation of the analysis is determined by the type of test substance and the conditions governing the focussing of the radiation. For example, the diameter of the focussed spot was 30 μm in one investigation[11], while other workers[7] investigated the distribution of hydrogen in the grains and in the intergranular boundaries of aluminium by interposing a diaphragm in the laser beam. The errors in the determination of the concentration of gases ranged from 5 to 25%, depending on their content and the nature of specimen. The scatter of the analytical results is apparently determined by the variations in the size of the sample evaporated per laser flash and can also be a consequence of the inhomogeneous distribution of the impurities in the specimens analysed.

Gaseous impurities in the bulk phase, in a surface layer approximately 50 μm thick, and on the surface of nickel have been studied[10] with a time-of-flight MSKh-3A mass-spectrometer using a laser to evaporate the sample material (radiation energy $E \simeq 2$ J, $\tau \simeq 0.5$ ms). The authors noted that, bearing in mind that the binding energy of the sorbed gases is approximately 10 kcal mole^{-1}, in a study of the surface desorption of gases one must employ a defocussed laser beam with $q \simeq 10^3$ W cm^{-2}. In this case, the surface gases are fully desorbed for only slight heating of the surface, which does not therefore entail the desorption of gases from the bulk phase. In an experimental test of the distribution of oxygen in the surface layer and in the bulk phase, nickel specimens were employed. The results of laser probing were compared with data obtained on etched plates by a dynamic method at 900°C. The comparison demonstrated a satisfactory agreement of the results obtained by the local and integral methods. The amount of gases (H_2, H_2O, $CO + N_2$, O_2, and CO_2) present in the surface layer exceeded by a factor of 2–3 their concentration in the bulk of the material. However, one should note that the application of a laser operating in the non-Q-switched mode has led[10] to unduly thick layers (~ 20 μm) removed per laser flash and the distribution of gases with respect to depth in the material could be investigated only very approximately. According to the authors' estimates, the sensitivity of the layer-by-layer analysis of gases was in the range 5×10^{-5}–1×10^{-4} wt.% and the reproducibility of the results was within approximately 50%.

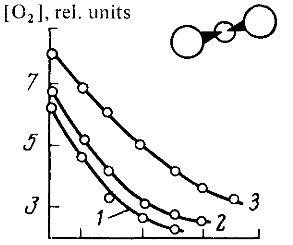

Figure 2. Curves for the distribution of oxygen with respect to the depth of the crystals after oxidation for 20 h at different temperatures (0°C): 1) 400; 2) 500; 3) 650.

The distribution of gases at different depths in the specimens has also been investigated in a study[13] where the distribution of oxygen in a cadmium telluride crystal was determined. These data (Fig. 2) are apparently of the same kind as obtained in another study[10], but similar curves are not quoted. Fig. 2 shows that the probing of the depth of specimens using a free running laser is restricted to a 20 μm region.

A novel problem, involving the study of the composition and partial pressures of the gases within the cavities of the 22KhS ceramic and also the study of its gas content due to its natural porosity, has been solved[18]. The authors note that the laser ($E \simeq 2$ J, $\tau \simeq 0.5$ ms) makes it possible to "open" cavities (0.5–1.2 mm in size) and pores in the ceramic material and cause the complete evolution of the gas contained therein, followed by its analysis on a time-of-flight mass-spectrometer. The experimental data obtained for the gas content in the cavities and pores led to the conclusion that the composition of the gases in the cavities differs somewhat from that in the pores in containing a higher proportion of carbon-containing gases. It was also established that the gas pressure varies linearly with the reciprocal of the radius of the defect.

Thus methods for local, rapid, and quantitative mass-spectrometric analysis of gases in elements[8,9], alloys[10,12], and chemical compounds[13,16] have been developed using a free running laser. The laser has been used in these studies to evaporate small (20–100 μm) sections of the specimen with subsequent ionisation of the evolved gas by an electron beam and the analysis of the ions on a time-of-flight mass-spectrometer of type MSKh-3A. Analysis based on the plotting of calibration curves makes it possible to investigate the distribution of gaseous impurities in the specimen.

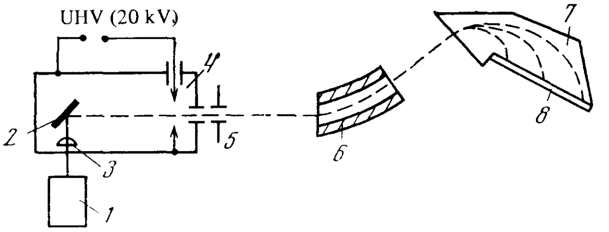

Figure 3. Schematic representation of the instrument with an analyser of the Mattach–Herzog type: 1) laser; 2) specimen; 3) focussing lens; 4) electrodes of the spark generator; 5) mass-spectrometer slit; 6) electrostatic analyser; 7) magnetic analyser; 8) recording plate.

The laser has been used[19–28] both for the evaporation and ionisation of chemical compounds. In this case, the resolving power of the mass-spectrometer (R) should be higher than in the analysis of light gases. Furthermore, in selecting the mass-spectrometric apparatus, it is necessary to take into account the considerable (~10 eV) scatter of the kinetic energies of the ionic component of the laser plasma and the complexity of the mass-spectra obtained[20,22–28]. Mass-spectrometers with an analyser of the Mattauch–Herzog type[19,25–28] (Fig. 3) having $R \geqslant 1000$ or with a time-of-flight analyser[20,22–24] having a resolution of approximately 100 have been used for the analysis. In order to obtain such resolution, the authors[20,22–24] achieved a monoenergetic ($\Delta T/T \ll 1$) ionic component of the laser plasma by accelerating it specifically using the electrodes of the ion source (Fig. 4). The detector could record both the ionic and neutral components of the plasma generated by the laser radiation. The spectra of neutral vapours have been obtained[20,22–24] following their ionisation by an electron beam with an energy of 15 eV, while other investigators[25–28] ionised the neutral component in a high-frequency spark discharge.

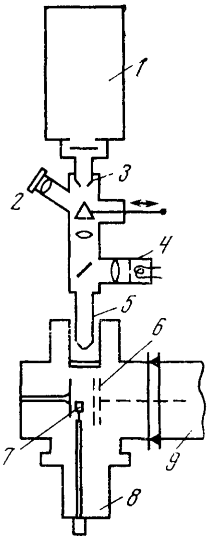

Figure 4. Schematic representation of the ion source: 1) ruby laser; 2) eye-piece; 3) diaphragm; 4) illuminator; 5) object lens; 6) accelerating grid; 7) specimen; 8) vacuum manipulator; 9) flight tube.

Studies have been made[20,22–24] on the products of the evaporation by the laser beam ($q \simeq 10^7$ W cm^{-2}) of Group VA and VIA elements, their intermetallic compounds[22–24], and also certain solid organic polymers[20]. It has been noted that the spectrum contains a large number of polyatomic ions of the elements and their compounds and that the number of polyatomic compounds in the mass-spectrum of the neutral component is greater than in the spectrum of the ionic component of the vapour. The results presented in these studies indicate a considerable difference between the laser and the usual (for example Knudsen) thermal evaporation. This difference is reflected in the type of polyatomic fragments constituting the vapour, the relative intensities, and the maximum number of atoms entering into the compound. The correlation between the type of polyatomic formations in the vapour and the structure of the condensed phase has been discussed[23,24]. It has been shown[24] that the structural difference between the polymorphic modifications of As_2O_3 is reflected in the type of polyatomic compounds present in the vapour. However, this relation has not been observed in all cases[22]. The relative intensities of the peaks of the polyatomic formations are in some instances unexpected. For example, Te_5, Sb_3, and Bi are the strongest ionic components in the vapours of tellurium, antimony, and bismuth respectively. In the experiments[30] on the usual thermal evaporation, these components are present in small amounts or are altogether absent. Fragmentation may occur in the vapour as a result of the high (close to critical) temperatures and pressures obtained in the zone where the laser radiation operates. The analytical characteristics of the apparatus are not indicated[20,22–24], but the Tables of the mass-spectra presented[20] show that the resolving power was approximately 100.

Mass-spectrometric studies of the plasma produced on evaporation of ferrites and semiconductor compounds of the type A(III)B(V) by a laser have been carried out[25,27]. When nickel ferrite ($NiO.Fe_2O_3$) is atomised, the ionic part of the vapour consists of products of the complete dissociation of its constituent oxides. Additional ionisation by a high-frequency spark does not affect the quantitative and qualitative compositions of the mass spectrum. The ratio of the intensities of the isotopic iron and nickel ions corresponds approximately to the stoichiometric formula of this ferrite. A study of yttrium ferrite ($(Y_2O_3).(Fe_2O_3)$) showed[25] that, together with the dissociation products (Fe,Y,O), oxygen-containing groups of atoms, in the first place YO and FeYO, are present in the mass spectrum. The ratio of the Y^+ and Fe^+ ionic currents deviates appreciably from that required by the stoichiometric formula. Additional ionisation by high-frequency sparks leads in this case to an appreciable redistribution of the ionic currents of the elements and compounds. It is believed[25] that the difference between the degrees of ionisation of iron and yttrium in the laser plasma can be accounted for by the difference between their ionisation potentials.

Analysis of intermetallic compounds of the type A(III)B(V) showed[27] that the Ga^+, As^+, and As_2^+ ions derived from gallium arsenide specimens and the Ga^+, P^+, and P_2^+ ions derived from gallium phosphide specimens predominate in the mass spectrum of the ionic component of the vapour. Ionisation of the neutral vapour causes an increase of the relative content of ions of the type As_n^+ and P_n^+, which the authors believe indicates the predominance of these species in the neutral part of the vapour. Comparison of the results of the laser and the usual thermal evaporation of compounds of the type A(III)B(V) leads to the conclusion that the degree of ionisation of gallium vapour following evaporation by laser radiation is much higher than in thermal evaporation. Lasers operating under specific conditions are preferable for the analysis of impurity concentrations averaged with respect to the volume of the specimen on a static mass-spectrometer of the Mattauch–Herzog type. For example, a laser with a radiation pulse frequency of 6.25 Hz has been used to analyse geological specimens[19]. Each pulse had $\tau \simeq 2.5 \times 10^{-4}$ s and $E \simeq 0.15$ J. The specimen analysed was moved automatically at a rate of 1 mm min^{-1}. The ion current generated by the laser radiation was 10^{-11} A, which, according to the authors, permitted analysis with a fairly short exposure time. The shape of the mass-spectrometric lines on the photographic plate was much more distinct than in the mass spectra obtained using a spark ion source. It was shown[19] that the presence of 5 wt.% of graphite increases the sensitivity of the method for certain elements (Si, Ti, and Fe), probably because the presence of carbon in the laser plasma promotes the dissociation of the metal–oxygen bonds. The concentrations of the majority of the impurities detected in the above study[19] (with the exception of alkali metals) were in the range 10^{-2}–10^{-3} at.%.

It is seen from the results quoted above that the published reports of investigations do not contain data on the coefficients of relative sensitivity for various (non-gaseous) impurities. There are no estimates of the lower limit at which impurities can be detected and of the accuracy of the results. Thus methods for quantitative mass-spectrometric analysis of non-gaseous impurities in solids using lasers operating under free running conditions have not so far been developed.

III. ANALYSIS USING A LASER OPERATING WITH A Q-SWITCHED RESONATOR (GIANT PULSE CONDITIONS)

When a giant laser pulse ($\tau \simeq 10^{-7}$–10^{-9} s, $q \geqslant 5 \times 10^8$ W cm^{-2}) acts on a solid, a highly ionised plasma is produced[2,3]. The diameter of the resulting crater is determined by the focussing conditions and its depth $H < 1$ μm depends on the type of substance and the power density in the laser beam.

The appreciable spread (0.5–2 k eV) of the initial energies of the ions formed when giant laser pulses act on a solid[3] makes many instruments with ordinary focussing unsuitable for mass-spectrometric analysis in this case. For example, the design of a time-of-flight mass-spectrometer with a laser ion source has been described[31], but its low resolving power (< 10), caused by the appreciable spread of the initial ion energies, apparently precludes its use for analytical mass-spectrometry. Calculations[32] for a time-of-flight mass-spectrometer with a laser source, designed for the analysis of gaseous mixtures in metals, showed that the high initial spread of the kinetic ion energies ($\Delta T \simeq 1000$ eV) requires an additional acceleration of the ion beam in order to achieve adequate mass resolution. The authors quote data for the time and amplitude characteristics of the accelerating potential pulses necessary to achieve a mass resolution of approximately 15. Theoretical estimates of the sensitivity of this instrument yield approximately 10^{-7}–10^{-8} at.% in the determination of gaseous impurities. However, allowance for the influence of the space charge of the ion beam apparently leads to an impairment of the analytical characteristics of the instrument compared with the calculated characteristics.

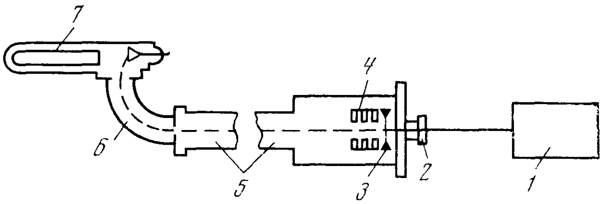

Figure 5. Schematic representation of the instrument with an energy analyser: 1) Q-switched laser; 2) object lens; 3) foil specimen; 4) single-potential lens; 5) flight space; 6) energy analyser; 7) scintillation detector.

In order to improve the resolution of the mass-spectrometer, an electrostatic analyser with a 90° deflection of the ion beam was placed[33] at the end of the flight tube (Fig. 5). Nevertheless, the resolving power of the instrument did not exceed 30. This is probably due to the high space charge in the ion beam. In order to improve the resolving power of the instrument (up to 90), some investigators[35-39] placed at the end of the flight tube (approximately 3 m long) an analyser with crossed electrostatic and magnetic fields (Fig. 6). The design of the instrument also made it possible to employ the electrostatic and magnetic analysers separately. A characteristic feature of the time-of-flight instrument used in some investigations[41-47] (Fig. 7) involves the use of the analytical component of a commercial MKh 1303 mass-spectrometer as the analyser. A resolution of 100 was obtained at the 5% level of the peak height. The fundamental analytical characteristics of the instrument employed[41-47] are as follows: lower limit of detection approximately 1×10^{-4} at.%, error of analysis 15% for an impurity concentration of approximately 10^{-2}%, information capacity[48] of the mass-spectrometer approximately 5×10^3 bits. The parameters of the laser radiation were $E \simeq 1$ J, $\tau \simeq 40$ ns, and $q \simeq 2 \times 10^9$ W cm^{-2}. The high density of the laser plasma[2,3] and the large scatter of the ion energies forced the investigators[35-39,41-47] to reject any ion-optical systems in the laser source. The ions spread throughout the flight tube with the energies which they acquired at the initial stage of the fragmentation of the condensed portion of the plasma. The lack of ion focussing and the considerable length of the flight space lead to an appreciable impairment of the transmission coefficient and hence to a decrease of sensitivity to approximately 10^{-5}–10^{-4} at.%.

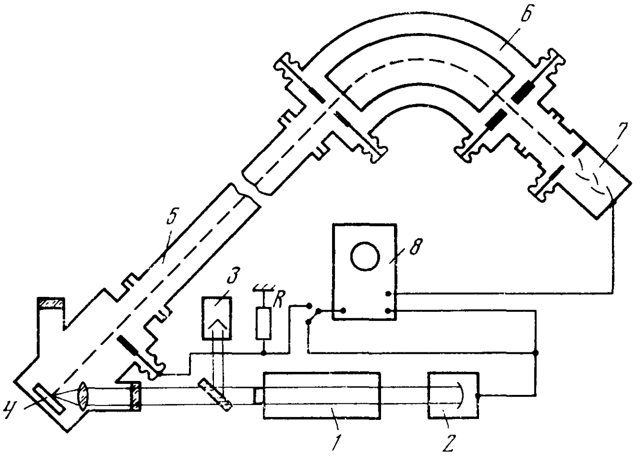

Figure 6. Schematic representation of the instrument with an analyser comprising cross electrostatic and magnetic fields: 1) laser; 2) photoelectric cell; 3) energy measuring device; 4) specimen; 5) time-of-flight analyser; 6) analyser with crossed electrostatic and magnetic fields; 7) secondary electron multiplier; 8) recording oscillograph.

When Q-switched lasers were used, several interesting analytical problems were solved. A Q-switched ruby laser ($\tau \simeq 30$ ns, $q \simeq 10^{10}$ W cm^{-2}) was used to evaporate and ionise thin specimens of a solid[33]. According to the authors' estimates, the efficiency of the ionisation of copper was 10^{-2} ions per atom. The ionisability of certain other thin metallic foils (Al, Fe, Ag, Au, and Li) was approximately the same with the exception of sodium and potassium films, the ionisability of which was higher. Apart from these substances, specimens of solutions of various substances, particularly metal nitrates, hydroxides, and chlorides, were also investigated. Copper and aluminium foils served as supports for these solutions. Peaks corresponding to singly charged and multicharged atomic ions only were observed in the resulting mass spectra. The ionisation efficiencies of various metals in such specimens were approximately the same, but for other components of the specimen, for example H, N, O and Cl, the differences between ionisabilities reached two orders of magnitude.

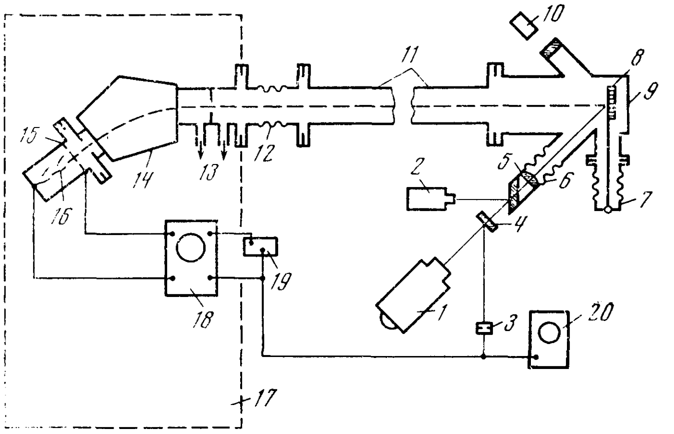

Figure 7. Schematic representation of the instrument with a magnetic analyser; 1) laser; 2) device measuring radiation energy; 3) photoelectric cell; 4) plane-parallel plate; 5) lens; 6) bellows; 7) vacuum manipulator; 8) cassette with specimens; 9) cover of ion source; 10) telescope; 11) flight tube; 12) mechanical compensator; 13) outlet to diffusion pumps; 14) magnetic analyser; 15) retarding potential grid; 16) secondary electron multiplier; 17) analytical section of the MKh-1303 instrument; 18) "Chronotron"; 19) G5-15 generator; 20) time interval measuring device.

The abundances of the isotopes of elements atomised by laser pulses ($\tau \simeq 40$ ns, $E \simeq 0.5$ J) have been measured[36]. The authors note that the accuracy of the determination of the isotope ratios (approximately 3% of the measured quantity) is lower than in measurements on instruments of the static type, because of the relatively low accuracy of the measurements which is in general characteristic of dynamic instruments. It was concluded that fast measurements of the isotopic abundances, restricted to a region limited mainly by the aberrations of the optical system and the divergence of the laser beam, may be made by the proposed method.

Analysis of lead, indium, and niobium specimens led to the detection of impurities[39] whose content in the lead specimen was approximately 10^{-4} at.%. The authors believe that the sensitivity of the instrument is sufficient to detect impurities at concentrations of approximately 10^{-5} at.%.

The possibility of investigating the elemental composition of multicomponent geological rocks has been reported[37]. The ion source used to evaporate and ionise the sample was a neodymium laser ($\tau \simeq 40$ ns, $q \simeq 4 \times 10^{10}$ W cm^{-2}). Comparison of the results with data from emission spectroscopic analysis showed that elements with low atomic weights can be more effectively determined on a laser mass-spectrometer. In order to determine the concentrations of the elements in geological rocks, the energy distributions of the detected ions were found from the experimental results. Integration of the distributions makes it possible, according to the authors, to obtain the average atomic concentrations of the elements present in the sample. However, this method of determining the concentrations of the elements is extremely laborious and unsuitable for local or layer-by-layer analysis of the impurities present in the specimen. It should also be noted that, in order to employ this method, it is necessary to make sure initially that the ionisations of the atoms of various substances under the influence of laser radiation with flux density $q \simeq 4 \times 10^{10}$ W cm^{-2} are equally probable.

The experimental determinations of the stoichiometric compositions of ionic crystals of the type $A_nB_mC_p$ have been published[38]. The power density of the laser emission was $q \simeq 2 \times 10^9$ W cm^{-2} in the analysis. The stoichiometry of the selected crystals was determined from the ratio of the peak heights for singly charged ions of the elements A, B, and C having an energy of 100 eV. This method for the determination of stoichiometry conflicts with other data[33], which, however, may be accounted for by the differences between the objects analysed in the two investigations[33,38] and also by the differences between the energies of the ions used for analysis†.

Using a time-of-flight mass spectrometer (with an electrostatic analyser to improve mass resolution) in combination with an "Arzni" laser, Kholodar' et al.[40] studied the distribution of carbon in silicon specimens. By scanning the surface of the specimen with a laser beam, they established that carbon may be present in the form of inclusions consisting (according to electron diffraction data) of the β-phase of silicon carbide. The size of the inclusions, determined by electron microscopy, is between 0.1 and 20 μm. The analytical characteristics of the mass-spectrometer are not quoted.

It is seen from the above results that the problem of the consistency between the composition of the substance in the solid phase and the composition of the ions formed from the solid under the influence of giant pulses of laser radiation was not studied in the above investigations[31-40]. The relevant reports do not therefore describe methods for the quantitative analysis of impurities in the elements and in the compounds, stating merely the possibility of the qualitative analysis of solids using laser ion sources. For a quantitative determination of impurities, it is necessary to know the coefficients of the relative sensitivity to impurities in different matrices, or the instrument must be calibrated against standards with known impurity contents, or analytical methods without standards must be developed‡.

In view of the foregoing considerations, the authors[41-46] concentrated attention on the justification of methods for the quantitative mass-spectrometric analysis of the elements using calibration graphs[42,43] and an internal standard[46] as well as the method of the layer-by-layer analysis[44,45,47] of solids with ionisation of the sample by giant laser pulses.

For the purpose of mass-spectrometric analysis using a laser ion source, it was necessary to elucidate the dependence of the ejected mass of the irradiated specimen (the sample size) on the concentration of its impurities. The upper limit of the impurity concentrations for which the mass ejected from specimens with a matrix of the given type changes under the influence of irradiation by giant laser pulses was studied using silicon, iron, and aluminium specimens with significantly different types of chemical bonds between the atoms in the lattice. The form and concentration of the impurities in these specimens were known. It was found[46] that the ejected mass is independent (within the limits of a 12% experimental error) of the content of impurities if the concentration of the latter does not exceed 9, 6, and 0.9 at.% for aluminium, iron, and silicon specimens respectively.

In the development of the method for the quantitative analysis of steel for carbon, manganese, and chromium, spectroscopic standards were used[43]. It was established that the dependence of the height of the mass-spectrometric peak of the impurity element on its concentration is linear. The sensitivity of the instrument to the impurity depends on its nature and can vary severalfold. The data used to plot calibration graphs for each impurity were reproduced several times and the slope (sensitivity) for each impurity did not vary with time. It was concluded that the sensitivity of the instrument to carbon in silicon is twice as high as the sensitivity to carbon in steel and approximately equal to the sensitivity to vanadium in steel. Consequently the sensitivity depends not only on the nature of the impurity element but also on the nature of the main substance. Thus, quantitative mass-spectrometric analysis of solids requires at least one standard of the same type as the specimen analysed.

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†The energy spectrum of the ions formed under the influence of giant laser pulses is complex (see, for example, Bykovskii et al.[60]) and the form of the spectrum has still not been fully explained. Unfortunately, the authors of the analytical studies do not by any means always state the energies of the ions used for analysis. The problems of the determination of the stoichiometric compositions of solid binary compounds have been investigated in greatest detail by I.D.Kovalev, N.V.Larin, and G.A.Maksimov [Letters to Zhur.Tekh.Fiz., 1, 798 (1975)] and by G.G.Devyatykh, I.D.Kovalev, N.V.Larin, and G.A.Maksimov [Dokl.Akad.Nauk SSSR, 226, 109 (1976)], whose papers were published after this review had been written.

‡The problems of the development of methods without standards are dealt with in the reports by I.D.Kovalev, G.A.Maksimov, and N.V.Larin ["XI Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii; Analiticheskaya Khimiya, Referaty Dokladov" (The XIth Mendeleev Congress of General and Applied Chemistry. Analytical Chemistry. Abstracts of Reports), Izd.Nauka, Moscow, 1975, p.110] and Yu.A.Bykovskii, G.I. Zhuravlev, L.M.Babenkov, T.A.Basova, X.I.Belousov, V.M.Gladskoi, V.V.Gorshkov, V.G.Degtyarev, and V.N.Nevolin [V Vsesoyuznaya Konferentsiya po Polucheniyu i Analizu Veshchestv Osoboi Chistoty, Gor'kii, Tezisy Dokladov" (The Vth All-Union Conference on the Preparation and Analysis of Specially Pure Substances, Gorky. Abstracts of Reports), Izd.Nauka, Moscow, 1976, p.125], which were published after this review had been written. The second communication reports the attainment of a detection limit of 10^{-7} at.%.

Despite its satisfactory accuracy (to within approximately 8%), the method of quantitative analysis using calibration graphs plotted from the determinations of impurities in standard specimens suffers from a number of disadvantages associated with the lack of standard specimens for different impurities in matrices of various types. For this reason, a method has been developed for quantitative mass-spectrometric analysis without standards[46]. In a study of the effect of giant laser pulses on the elements, the authors established that, for these substances, the number of ejected atoms (N), the yield of ions (n^+), and the ionisability ($\epsilon = n^+/N$) have a periodic relation to the atomic number of the element. The absolute ionisability of iron, for example, is 1.4%§, which is close to the value of Fenner and Daly[33]. It has been shown that the ratio of the ionisability of the impurity to the ionisability of the matrix is equal to the coefficient of relative sensitivity[49] in mass-spectrometric analysis¶. Depending on the nature of the material of the matrix and the impurity, the above coefficient can vary by a factor of ten[46]. A method for the quantitative analysis of the elements using an internal standard, which is the substance of the matrix of the given specimen, has been developed on the basis of these data.

Since the coefficient of relative sensitivity K for many pairs of elements is unknown, a formula has been proposed[46] for the estimation of this quantity:

$$K = \frac{\Delta Q_0 \varphi_i \sigma_0^2}{\Delta Q_i \varphi_0 \sigma_i^2}\ , \qquad (1)$$

where ΔQ is the heat of sublimation, φ the ionisation potential, σ the cross-section for the ionisation of the atoms by electrons, and the subscripts i and 0 refer to the corresponding impurity element and the matrix. For the majority of the elements, the calculated and experimental data are in satisfactory agreement.

The results of the analysis of the impurities in various standard steels, specimens of silicon, chromium, germanium, copper, and aluminium indicate the possibility of employing the method with an internal standard. The accuracy of the analysis is to within approximately 15% for an impurity concentration of approximately 10^{-2} at.% and the lower limit of the detection of impurities is 10^{-4}–10^{-3} at.%, depending on the nature of the impurity and the main substance.

The effect of the giant laser radiation pulse on the solid leads to the appearance of a crater at the point of the interaction of the laser beam with the surface of the specimen[3]. The average thickness (H) of the layer of substance removed by one laser pulse has been determined[45] from the results of Devyatykh et al.[41] The results of the calculation of H are presented in the Table with a relative error not exceeding 20%. The thicknesses of the layers removed from the majority of elements are not quoted in the literature, but the values of H for silicon agree satisfactorily with the data of Grevtsev et al.[50] The determination of H for different energy densities of the laser beam showed that an increase of the energy density from 0.35×10^2 to 1.6×10^2 J cm^{-2} leads to an increase of the thickness of the layer removed by a factor of 2–4.

The average thicknesses (H) of the layer removed for a radiation energy of 1 J, area exposed to radiation $S = 1 \times 10^{-2}$ cm^2, and a pulse duration of 40 ns.

Element	H, µm	Element	H, µm
C(graphite)	3.22	Zn	0.53
Al	0.7	Ge	1.92
Si	1.49	Zr	0.37
Mg	1.08	Nb	0.16
V	0.29	Mo	0.17
Cr	0.25	Ag	0.51
Fe	0.42	Cd	0.64
Ni	0.45	Sn	2.19
Cu	0.21		

The concentrations of the impurities detected in the layer of substance can be determined from the mass spectrum. The lower limit of the detection of impurities in the layer-by-layer analysis is at the level of 10^{-4} at.% and can vary over a factor of ten depending on the ionisability of the matrix and the impurity; the error of the measurements is approximately 25%. The spatial resolution with respect to depth in the method involving the laser probing of solids is at least 0.5 µm for the majority of the substances investigated (see Table). For iron, niobium, molybdenum, and many other transition metals, the resolution with respect to the depth of the layers removed reaches 0.05 µm for an energy density of the giant laser pulse of approximately 0.35×10^2 J cm^{-2}. The layer-by-layer analytical method has been used[47] to investigate the distribution of carbon in chromium films. It is seen from the results that the employment of giant laser pulses to evaporate and ionise a sample in the ion source of the mass spectrometer makes it possible to take into account the distribution of impurities in thin layers of solids.

Taking into account the above features, the use in mass spectrometry of lasers working under giant pulse conditions may be regarded as promising for the determination of the average content of impurities and for the elucidation of their distribution with respect to depth and on the surface of solids†.

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§The dense plasma formed under the influence of giant laser pulses is almost fully ionised ($\epsilon \simeq 100\%$). However, at the end of the laser pulse, there is sufficient time for the dispersal of only a small part (n^+) of the peripheral ions. The so called "quenching" of the degree of ionisation is observed for ions of this kind[60]. These ions can in fact be recorded in mass-spectrometric analysis. The remaining ions on the inner part of the concentrated region of the plasma recombine almost completely to neutral atoms within distances of the order of the initial size of the plasma[61]. Attempts to remove all the ions from the concentrated part of the plasma have not so far been described in the literature.

¶Ions corresponding to the high-energy maximum[60] in the energy distribution for the given element have been used for analysis[41–47].

†The report by S.V.Gaponov, I.D.Kovalev, V.I.Luchin, G.A.Maksimov, L.I.Pontus, and A.I.Suchkov in "V Vsesoyuznaya Konferentsiya po Polucheniyu i Analizu Veshchestv Osoboi Chistoty, Gor'kii, Tezisy Dokladov" (The Vth All-Union Conference on the Preparation and Analysis of Specially Pure Substances, Gorky. Abstracts of Reports), Izd.Nauka, Moscow, 1976, p.132, was published after this review had been written. The authors obtained a focussed spot 15 µm in diameter, which enabled them to investigate the distribution of microinclusions in solids.

IV. COMPARATIVE CHARACTERISTICS OF LASER, SPARK, AND THERMIONIC ION SOURCES USED IN THE MASS-SPECTROMETRIC ANALYSIS OF SOLIDS

An ion source with surface ionisation (a thermionic source) was proposed for mass-spectrometers by Dempster in 1918. In 1936, he developed methods for obtaining ions based on the electrical breakdown of the interelectrode gap *in vacuo* (spark ion source). The first publications[4-6] on the use of lasers in the ion sources of mass-spectrometers appeared in 1963. A monograph dealing with the mass-spectrometric methods using ion sources with electric discharges[53] states that the authors included in the book a chapter on a laser source which successfully supplements the technique employing a spark source. It is also noted in this monograph that the available information about laser sources is at present inadequate. The comparative characteristics of the thermionic, spark, and laser mass-spectrometric methods are described below. The source with secondary ion–ion emission has been excluded from consideration, because quantitative analytical methods have not so far been developed for this method of obtaining ions from a solid.

When the surface of a metal with the electron work function φ and the first ionisation potential I is heated to a certain temperature, there is a definite probability of evaporation of positive and negative ions together with neutral species. The relative intensities of the fluxes of positive ions n^+ and neutral atoms n^0 are defined by the Sacha–Langmuir equation (see, for example, Kaminsky[54]). The ionisation efficiency varies exponentially with the difference between the electron work function and the ionisation potential. For alkali metals on the surface of tungsten, $\varphi - I > 0$ and the ionisation efficiency in evaporation is approximately unity. If the difference $\varphi - I < 0$, which occurs with the majority of elements, the ratio n^+/n^0 decreases[1] to 10^{-6}. In order to employ the thermionic emission effect in mass-spectrometry, ion sources with one or three tungsten filaments[1,54] and a crucible ion source[55] are used. The mass-spectrometers of types MI 1305, MI 1308, MI 1309, MI 1310, and MI 1311 produced in the USSR are nowadays equipped with three-filament ion sources with surface ionisation.

Three types of sources can be distinguished in accordance with the method used to achieve the electrical breakdown of the vacuum gap[1,49]: the high-frequency spark source, the source of the "vacuum vibrator" type, and the low-voltage source. The high-frequency spark source has been used most frequently in analytical mass-spectrometry. It has been shown in a report by Gorman[56] and in many subsequent publications that the efficiencies of the ionisation of the atoms of various elements are different in the high-frequency spark source. The quantity characterising this difference is the coefficient of relative sensitivity K which is determined empirically using standard specimens. Extensive data on the determination of relative sensitivity coefficients have been compiled in a monograph[49]; it has been noted that K remains constant for a wide range of impurity concentrations in the matrix investigated. The same applies to a laser ion source[43,46]. In the spark source, the differences between the relative sensitivity coefficients for a given impurity in different matrices can reach an order of magnitude. For example K for indium[49] is 1.1 in iron and 9.2 in zinc. The differences between the values of K for a laser source[46] are of the same order of magnitude‡. Consequently, when no account is taken of the corrections introduced by the coefficient of relative sensitivity, the error in the determination of the concentration (for both spark and laser sources) may reach 1000%. Since the values of K for all impurities in different substances cannot be obtained experimentally, attempts have been made in spark mass-spectrometry to determine them from certain physical parameters characterising the substance. The best agreement with experiment is given by the calculation of K from the formula[49] $K = \sigma/\Delta Q\varphi^4$, where σ is the effective ionisation cross-section of the atom, ΔQ the heat of sublimation, and φ the ionisation potential. Comparison of the above relation with Eqn. (1) demonstrates some similarity between the evaporation and ionisation processes when the substance is acted upon by the laser radiation and the "spark".

Thus the differences between the ionisabilities of the atoms of various elements in spark and laser sources are an order of magnitude. A much higher selectivity in the ionisation of the substance is characteristic of the thermionic source, the difference between the ionisation efficiencies reaching in this case six orders of magnitude. However, in view of the limitations of the thermionic emission method associated with the difficulty of preparing the samples for analysis, the possibility of their contamination, and the effect of the "memory" of the thermionic source[57], the authors of a monograph[52] note that the method is not universally applicable in mass-spectrometry.

The sensitivity of the analysis by spark mass-spectrometry is 10^{-5}–10^{-7} at.%.[1,49,53] The sensitivity of the determination of impurities when a laser ion source is used amounts to 10^{-4}–10^{-5} at.%, but the comparatively low sensitivity of the laser method can be explained by the inadequacy of the ion-optical systems of the mass spectrometers§ which have been used in combination with this ion source; there was no ion-optical arrangement directly in the source[33-46]. In the thermionic emission method, the sensitivity of detection is 10^{-5}–10^{-7} at.% only for alkali metals, while for the majority of other elements it is less satisfactory by several orders of magnitude[1,57].

The formation of ions in the laser source is probably more efficient than in the spark source. Thus it has been stated[49] that, in order to detect an impurity at the level 10^{-3} at.% in substances with a high atomic weight, the volume of the specimen which must be atomised in the ion source is approximately 3×10^{-5} cm^3. This corresponds (for average densities of the substance $\rho \simeq 5$–6 g cm^{-3}) to the atomisation of a mass of approximately 2×10^{-4} g. The ejection of such a mass may be achieved only for comparatively long exposures to the spark. In a laser ion source, impurities at a concentration of 10^{-3} at.% can be detected after a single exposure to a giant laser pulse. The ejected mass does not then exceed 10^{-6} g for the majority of substances. The integral ion current generated under the influence of a single laser radiation pulse is then > 1 A. The coefficient of the ionisation efficiency is $n^+/n^0 \simeq 10^{-2}$. The corresponding currents for spark ion sources are not quoted in the literature.

The comparatively long exposures to the spark required to detect an impurity at a level $\geqslant 10^{-3}$ at.% hinder to a large extent local layer-by-layer analysis of solids. The scope of the laser ion source for local layer-by-layer analysis is characterised by average thicknesses of the layer removed by a single layer pulse (see Table). The size of the spot in analysis using a laser reaches 10^{-5} cm^2

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‡ See the second footnote to Russ. p. 2131.

§ See the first footnote to Russ. p. 2130.

and the ease with which a given section of the surface to be irradiated is selected makes it possible to investigate, for example, the distribution of gases in the grains and along the intergranular boundaries of metals. For the above reasons, the method of layer-by-layer analysis using a laser[45] is simpler than the corresponding method using a spark ion source[58]. There are no methods of layer-by-layer analysis using a thermionic source.

The spark ion source does not apparently allow experiments designed to investigate the surface sorption of gases. The application of a laser makes it possible to investigate the composition of the gases sorbed on the surface, since giant laser pulses with $q \simeq 10^7$ W cm^{-2} do not disrupt the specimen but do eliminate the gases present on the surface of the sample[45,59].

The employment of a laser in the ion source permits a rapid determination of the composition of the substance. The time consumed in obtaining the complete mass-spectrum of the impurities in the substances analysed does not exceed 2–5 min. When the spark source is used, the time is several hours. The simple structure of laser mass spectra (giant pulses), consisting of the lines corresponding to singly and multiply charged atomic ions[35,46], permits a rapid interpretation of the spectrogram, while the structure of the spark mass-spectra is very complex[1,49,53]. The lines recorded in the spectrum correspond to a wide variety of multiply charged and polyatomic ions. The number of lines depends on the number of isotopes of the element, its physical properties, and the parameters of the spark discharge. The mass-spectrum always contains lines due to the ionisation of the residual gases. In order to take into account the organic impurities and to make sure that the lines of the multiply charged and polyatomic ions detected in the mass-spectrum do not overlap, the analytical lines of the impurities, the resolving power of the mass-spectrometer must be fairly high ($\geqslant$ 1000).

In analysis using a laser ion source, it is in fact immaterial whether the test specimen is a conductor, a dielectric, or a semiconductor. Analysis of dielectric materials and geological rocks on a mass-spectrometer with a spark ion source requires fairly complex preliminary operations owing to the impossibility of the direct analysis of non-conducting solids in a spark source. Analysis of dielectrics is based on the application of special "igniting" electrodes (probes) made of conducting high-purity materials. The electrodes for the analysis of non-conducting powders are made by packing the samples into metallic tubes, by pressing them with added graphite powder, or by sputtering films of the dielectric investigated onto metallic electrodes[49]. The complexity of the spark mass-spectra is in this case aggravated by lines due to the conducting additives introduced into the substance analysed.

The error in the determination of the concentration of impurities using a laser ion source is 12–15%, which corresponds approximately to the errors in spark mass-spectrometry[49]. Such non-reproducibility of the results is caused mainly by the scatter in the parameters of the laser radiation pulses. The rapid development of laser techniques gives rise to the hope that in the immediate future the characteristics of the lasers will be improved and that this will increase the accuracy of the results obtained on mass-spectrometers with laser ion sources.

The characteristics of laser ion sources described above indicate the possibility of extending the range of problems soluble by the mass-spectrometric analysis of solids as well as good prospects for the development of the mass-spectrometric analytical method using laser ion sources.

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The Chemical Aspect of Exoemission

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The results of studies on exoemission employing various excitation procedures are examined from the single standpoint of physicochemical reactions on the surfaces of solids. The prospects for the application of exoemission in scientific research and in engineering are discussed.
The bibliography includes 164 references.

CONTENTS

I. THE PROBLEM OF EXOEMISSION

Exoemission is a new type of emission of negative charges—slow electrons and ions—together with thermal emission, autoemission, photoemission, and secondary emission. In contrast to the types of emission known previously, it appears after a solid has been subjected to various influences inducing the formation of excited states and exhibits an appreciable inertia. On subsequent heating in the pre-Richardson region, the emission exhibits a number of peaks characterising the energy spectrum of the charge localisation levels on the surface.

The emission may be excited either by physicochemical reactions in the surface layers accompanying adsorption (desorption), oxidation, corrosion, and catalytic processes, phase transformations, etc. or as a result of external influences—mechanical, radiation, etc. Since emission occurs at low temperatures, the emitting surface may be assumed to be in a thermodynamic non-equilibrium state and to retain the properties resulting from its previous history. This gives rise to the prospect of employing exoemission in the study of physicochemical processes on the surface.

Detailed investigation of this effect began with Kramer's studies in 1950.[1] Despite the publication of numerous reports, particularly in recent years[2], exoemission continues to remain a relatively little investigated phenomenon, which is considered only by a limited circle of physicists.

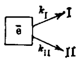
There is at present no theory whereby one could explain from a single standpoint the emission from metals and non-metallic crystals, semiconductors, and dielectrics. Kramer[1] suggested that mechanical influences on the surface of metals result in the formation of an amorphous phase (the Beilby layer) and that the emission is a consequence of the exothermic transformation during its recrystallisation. This hypothesis still stands, but the effect described by Kramer has been called "exoelectron emission" (The First International Symposium, Innsbruck, 1957).[3] Unfortunately there is a confusion in terminology and the individual types of manifestation of exoemission are referred to as "chemoemission",[4] stimulated emission[5], sorption emission[6], and low-temperature emission[7]. This situation merely complicates the development of a single mechanism of this phenomenon and hinders mutual understanding between teams of research workers concerned with the problem of exoemission.

In order to explain exoemission from metals, a hypothesis has been put forward[8] according to which electrons are emitted as a result of the heat of adsorption of active gases and the peaks of the thermally stimulated emission correspond to centres with different adsorption potentials.

The problem of the nature of emission from ionic crystals—crystalline phosphors and coloured alkali metal halides for which electron energy level schemes have been developed fairly satisfactorily—has been investigated to the greatest extent. The majority of studies in this field are based on the experimental analogy between the phenomena of exoemission and luminescence and are directed to the investigation of the physical aspect of this phenomenon[1,9-12]. According to the most general Bohun-Nassenstein theory[10,12], the electrons entering the conductivity band on excitation are localised at shallow capture levels. After the removal of excitation, the trapping levels are gradually vacated owing to thermal energy with transfer of electrons via the conductivity band outside the limits of the crystal—afteremission is observed or, when the electrons enter activator levels, there is an afterglow (phosphorescence). Decaying afteremission frequently occurs only on stimulation with light and in this case the emission is said to be photostimulated. In a number of studies it has been assumed[13] that the thermally stimulated emission (TSE) and the photo-stimulated emission (PSE) are two different phenomena involving different mechanisms, which should be considered separately.

The afteremission phenomena are due to the relaxation processes of the excited states and in the general case can be described by a sum of exponential terms or by the empirical law $I \propto I_0 t^{-n}$, where $n \simeq 1$. When the temperature is increased uniformly, deeper levels are vacated—thermally stimulated emission is observed with a set of maxima corresponding to localisation levels of different depths. For the analysis of the energy spectrum of the capture levels, the mathematical procedures of the theory of luminescence developed by Randall and Wilkins[14] are used. In the mathematical treatment of exoemission kinetics, one usually calculates the depth of the localisation levels (more precisely the activation energy for the release of electrons) and the pre-exponential factor. A very thorough critical review of studies concerning the kinetic analysis of exoemission phenomena has been published[15]. The authors note the deficiencies of the mathematical procedure of the luminescence theory (of Randall and Wilkins, Lushchik, etc.) and its modification in relation to calculations of the depth of the localisation levels of exoelectrons[14,16]. A method has been proposed for the analysis of the complex spectra of thermally stimulated emission when several unresolved peaks are superimposed. The possibility of resolving the TSE peaks and of determining their parameters has been demonstrated. Similar problems are being solved in the theory of thermal luminescence and in the analysis of thermal desorption spectra.

On the basis of "physical considerations", exoemission has been considered[15] as one of the possible channels for the relaxation of excited solids. The simplified relaxation mechanism proposed by the above workers is given below:



exoemission or thermal luminescence

other channels for relaxation involving the same capture centre.

The results of non-isothermal experiments undertaken in the study of thermally stimulated emission, thermal luminescence, etc. led to a method for the interpretation of experimental data[17] whereby one can determine the parameters of the two processes involved in the mechanism. Recommendations have been made for computer calculations on the kinetics of relaxation processes (programming). The authors note that the correct determination of the kinetic parameters by any of the methods described in the literature is then possible only when account is taken of the multichannel processes in relaxation. According to Burkhanova et al.,[15] the proposed mathematical models are of interest for the construction of a physical picture of the relaxation; they have been analysed in detail[15] and will therefore not be considered in the present review.

Thermally stimulated emission takes place as a result of the thermal liberation of negative charges in the pre-Richardson region when the energy of the electrons in the state of thermodynamic equilibrium is insufficient to overcome the surface potential. Photo-stimulated emission takes place under the influence of light with a wavelength exceeding the red limit of the photoeffect. Thus the phenomena considered are observed in the region of stimulating influences below the threshold values for thermal emission and photoemission and one of the central problems of the theory is the origin of the energy required for the release of electrons.

It has been suggested[18,19] that the energy required for the release of electrons is supplied by electron–hole recombination processes in transitions between the bands ("Auger recombinations"). This energy is transferred, for example, by the exciton mechanism, to the electrons localised at shallow capture levels near the surface. According to Bohun, only the high-energy component of the Maxwellian distribution of conductivity electrons is emitted (in the author's terminology[19], the "Maxwell tail theory"). It is noted that the "Auger mechanism" is valid only for dielectrics, where the width of the forbidden gap exceeds the electron affinity of the crystal, but does not explain the emission from semiconductors.

Assuming that TSE is a quasistationary process, Bohun[14] combines the equations of thermionic emission and thermoluminescence and obtains expressions describing the experimental data for emission from coloured or activated alkali metal halides.

The mathematical models for calculations on exoemission kinetics, based on the most general physical concepts, make it possible, according to Burkhanova et al.,[15] to determine the energy spectrum of the surface traps; the role of the surface potential in the exoemission phenomena is not discussed in this connection. The mathematical apparatus of Bohun's theory[14] represents the electron liberation processes as processes in which the surface potential is overcome. The role of the electron work function (electron affinity) has been considered theoretically also in a number of other studies[20], but the experimental results concerning the influence of the surface potential on the exoemission parameters are contradictory.

It has been established[21] that the intensity maxima of thermally stimulated emission from certain metals correspond to the minimum electron work functions and exoemission has been suggested[22] as a method for the determination of the surface potential. An unambiguous correspondence between the parameters of exoemission and the electron work function has not been found in recently published investigations[23,24]: the emission capacity can increase after both a decrease and an increase of the electron work function. The results make it necessary to approach with even greater caution the interpretation of the results of studies on exoemission from the standpoint of the band theory of solids. Analysis of the available data shows that the fundamental exoemission parameters (decay constants, the number and positions of the peaks on the temperature curves characterising the spectrum of the energy states on the surface) are not determined by the nature of the emitting substance—the width of the forbidden gap, the type of conductivity, the nature of the chemical bond, and whether or not the substances are semiconductors or dielectrics, metals, oxides, or salts[25].

In view of the presence of non-compensated bonds, the surface of a real solid is known to be always covered by adsorption layers, particularly water. Since emission takes place from shallow surface layers, the adsorption film should play a significant role in emission processes. A phenomenological theory of the origin of exoemission has been proposed[25]. It is based on the interpretation of the physicochemical processes accompanying the formation and relaxation of the excited states in surface layers in the presence of adsorption films.

The chemical aspect of exoemission is considered in the present review. Various types of manifestation of emission accompanying the physicochemical processes on the surface or arising as a result of external influences are discussed. The results are considered from the single standpoint of the physicochemical reactions accompanying the relaxation processes in the damaged surface layer.

II. EXPERIMENTAL METHODS FOR THE INVESTIGATION OF EXOEMISSION

In view of the low currents (10^{-17}–10^{-19} A), exoemission is studied under conditions where individual pulses are counted. Geiger counters or secondary electron multipliers (SEM) are used in combination with standard radiometric apparatus[26]. Since the exoelectron energies are small (from a few tenths of an electron-volt to several electron-volts), the electrons do not pass through the mica window and the emitter must be placed within the counter. The designs of special counters of this type have been described[27]. Some investigators use closed counters applying an accelerating potential before the inlet window[28]. Gas-flow counters are more convenient and reliable. The working plateau (500 V) hardly changes when the temperature is raised to 400°C.[29] The application of an accelerating potential to the grid over the specimen constitutes a significant improvement to the operation of the counters; this not only increases the sensitivity but also reduces the scatter of the results.

In experiments with gas-filled counters, it is impossible to investigate the role in exoemission of physicochemical factors due to adsorption-desorption, catalytic, and other processes. The development of the chemical aspect of exoemission has become possible after secondary electron multipliers of the open type have been devised and high and ultrahigh vacuum techniques have been employed. The method of the physicochemical investigation of exoemission developed in a number of studies[25,30,31] involves special "cleaning" of the emitter in a high or ultrahigh vacuum and simulation of the emitting surface by the adsorption of the corresponding gases and vapours under controlled conditions.

The autoradiographic method, based on the familiar Russell effect[32,33], is used for the analysis of structural changes under mechanical influences. This method is not suitable for studies *in vacuo* and its sensitivity is low. An image of the structure of a high quality surface was obtained after the development of channel multipliers. Microchannel plates, consisting of a system of close-packed channel multipliers, make it possible to obtain directly the image of the emitting surface. An exoemission microscope has been developed on the basis of microchannel plates[34,35].

Studies *in vacuo* using a secondary electron multiplier with application of a deflecting magnetic field established the occurrence of the emission of negative ions together with that of electrons[36-38]; the ionic component was observed only in TSE measurements on substances containing adsorption layers. It therefore appears useful to replace the generally accepted term "exoelectron emission" by the term "exoemission".

Numerous studies dealing with the distribution of exoelectron energies have been published recently. The average energy of the electrons emitted after Emery powder has been ground is 0.65 eV.[39] The most probable energy of the electrons in the afteremission from BeO caused by electron bombardment is 0.1 eV.[40] A Maxwellian distribution of electrons, with average energies amounting to a few tenths of an electron-volt, has been found for photostimulated emission from K_2SO_4.[41] It was noted that the electron energy depends on the accelerating potential, the charge acquired by the specimen as a result of the emission, the optical stimulation energy, temperature, and the presence of adsorption layers. A study has been devoted[42] to special problems of the influence of the charging of the specimen surface, occurring both on excitation and as a result of emission processes, on the distribution of exoelectron energy.

The average energy of the emitted electrons in thermally stimulated emission from $BaSO_4$ ($t_{max} = 160°C$) was 1.1 eV, only 10% of the electrons had an energy of 2.7 eV, 1% had an energy of 5 eV, and the energy of 0.1% was greater than 8 eV.[43] The average exo-electron energies for TSE from ceramic BeO specimens were 0.5 eV.[44] The energy distribution depended on the technology of the manufacture of the ceramic; for $t_{max} = 250°C$, the maximum electron energy varied from 1.5 to 16 eV. Even higher energies (up to 80 eV) were found[45] for thermally stimulated emission from the surface of oxidised silicon. It is noteworthy that such high electron energies cannot be achieved, for example, as a result of exothermic chemical reactions, Auger recombination processes, or the emission of the high-energy component of the Maxwellian distribution, i.e. they cannot be understood on the basis of the available models of the origin of exoemission[18,19]. In order to account for the high electron energies, a theory was proposed[45] postulating the possibility of the acceleration of electrons in the strong field of the electrical double layer comprising the dielectric—the oxide covering the semiconductor. However, it is possible that the high electron energies observed by the authors are due to methodological errors.

A study of TSE from LiF specimens showed that a Maxwellian distribution of exoelectron energies occurs only at temperatures ≤ 100°C; with increase of temperature, deviations from the Maxwell law are observed. The authors note that the interpretation of the energy measurements in terms of the approximate equations of thermionic emission must be treated with caution. Studies on the distribution of the energies of exoelectrons from an aluminium surface (TSE)[47] also showed that the average energies and their temperature dependence are inconsistent with the exoemission models based on the band theory and the thermionic emission approximations.

III. EXOEMISSION ACCOMPANYING PHYSICOCHEMICAL PROCESSES

1. Emission in Adsorption and Oxidation of Metals

Studies under conditions of high and ultrahigh vacuum have now established that atomically clean metal and semiconductor surfaces lack exoemission capacity[48-50]. When active gases are admitted, particularly oxygen and water vapour, an intense emission of negative charges is observed. It has been established that the occurrence of the emission accompanying adsorption and oxidation requires photostimulation[48], but in some studies such emission has been observed in the dark[51].

A freshly formed layer of aluminium *in vacuo* ($p \simeq 10^{-7}$ mmHg) does not emit electrons. When oxygen is admitted ($p \simeq 10^{-5}$ mmHg), emission, decaying over a period of time, takes place[52]; in order to excite the emission, a continuous incidence of oxygen molecules on the surface is necessary. The emission in the adsorption of oxygen on a nickel film sputtered under ultrahigh vacuum conditions ($p \simeq 10^{-10}$ mmHg) has been studied[53]. Each successive admission of oxygen is accompanied by an emission flash, whose "yield" is 10^{-10} electrons per molecule. At room temperature the emission intensity initially decreases and then rises again, the number of emitted electrons depending strongly on the time interval between the successive doses of oxygen. The observed phenomena are explained by the gradual incorporation of the adsorbed molecules in the lattice, which terminates in several minutes; according to approximate estimates, two oxygen monolayers are sorbed. Similar processes occur when oxygen is sorbed by atomically clean tungsten and copper surfaces[53].

In some studies, an atomically clean metallic surface was formed as a result of the removal of oxide by milling[48,49,54]. The admission of oxygen at a specified pressure (5×10^{-5} mmHg) to a zinc surface cleaned with a steel brush gives rise to emission, whose intensity passes through a maximum[54]. A similar result was obtained for zinc and aluminium under ultra-high vacuum conditions[48].

The residual gas pressure has a significant influence on two factors: the time interval elapsed after cleaning the surface before the appearance of the maximum and the intensity of the latter (Fig. 1). After the maximum, the emission intensity diminishes exponentially; at a residual pressure $p \simeq 1 \times 10^{-8}$ mmHg, neither dark nor photostimulated emission was observed in the course of 10 min. Comparison of the time required for the appearance of the emission maximum (τ'_{max}) and the time required for the formation of a monolayer (τ'') showed that τ'_{max} exceeds τ'' by a factor of 10^3–10^4. The results were examined taking into account the Cabrerr–Mott mechanism of the oxidation of metals and it was concluded that the exoemission is not associated with the adsorption step but is due to a slower process—the initial oxidation stage. A shift of the limit of the photoeffect to the long-wavelength region in adsorption and oxidation takes place according to some investigators[48,49], owing to the decrease of the photoelectron work function of the oxide layer formed, although the corresponding measurements of φ were not made.

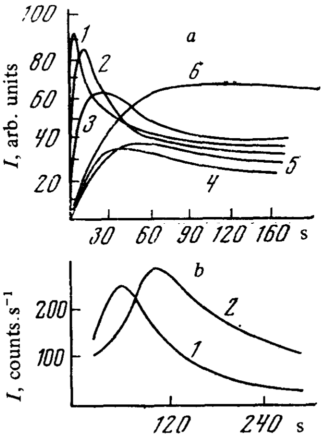


Figure 1. Time variation of the PSE intensity: *a*) from a zinc surface after cleaning at different residual gas pressures[49] [pressure (mmHg): 1) 5; 2) 3; 3) 2; 4) 1; 5) 0.7; 6) 0.2]; *b*) from an aluminium surface after mechanical treatment by impact[60] [time (min): 1) 1; 2) 4].

Simultaneous studies on photostimulated emission and the surface potential in the oxidation of metals have been made by Gel'man and Fainshtein[55]. The surface was cleaned in air and the emission was recorded by means of an open proportional counter. An increase of the surface potential φ corresponded to a fall of the PSE intensity I in the initial stage of oxidation; after a further growth of the oxide layer, the emission intensity increased and passed through a maximum and the correspondence between I and φ broke down. Since the experiments described were performed under non-controlled conditions, it is difficult to interpret the results, in particular it is impossible to take into account the role of the adsorbed water and oxygen.

Measurements of PSE and of the surface potential under controlled conditions with the aluminium surface cleaned in an ultrahigh vacuum were carried out by Linke and Born[56]. At a residual pressure $p < 10^{-5}$ mmHg, the emission intensity passed through a maximum after the surface had been cleaned, as in other studies[49,54]. In an ultrahigh vacuum ($p \simeq 10^{-10}$ mmHg), PSE was not observed even after a very vigorous mechanical treatment. Emission did not appear even after several hours following the admission of oxygen ($p \simeq 10^{-4}$ mmHg). It was found that the presence of adsorbed water is necessary for the appearance of PSE. Fig. 2 illustrates the variation of the "tribophotostimulated" emission from an aluminium surface in an atmosphere of water vapour and oxygen. In the former case, the emission intensity increased to a limit, falling after the next admission of oxygen. The authors[56] believe that, in the case of metals coated by adsorbed layers with a thickness of several angstroms, PSE represents photoemission of electrons from the metal; here the shift of the limit of the photoeffect occurs as a result of changes in electron work function in the presence of adsorbed molecules. This conclusion was confirmed by direct measurements of the photoelectron work function by Fowler's method. The admission of water reduced φ from 4.5 to 3 eV and led to the appearance of emission following illumination with red light.

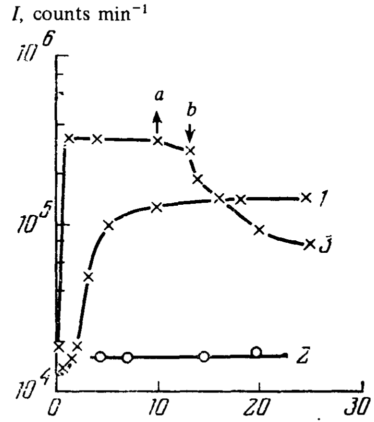


Figure 2. Time variation of the intensity of PSE from an aluminium surface after cleaning in different atmospheres: 1) H_2O (7.5×10^{-8} mmHg); 2) O_2 (8×10^{-8} mmHg); 3) H_2O (1×10^{-6} mmHg); *a*) evacuation; *b*) admission of O_2 (4×10^{-6} mmHg).[56]

The experiments described above led to a second fundamental conclusion[56]: the structural defects generated by mechanical treatment do not form emission centres in the absence of adsorbed layers. This postulate is consistent with Scharmann and Seibert's data[48] and demonstrates the lack of validity of the view of some investigators on the nature of exoemission from deformed metals, who failed to take into account the decisive role of the physical chemistry of the surface in exoelectron emission processes[57-60].

2. Thermally Stimulated Emission in Desorption

For the majority of substances investigated—metals, elementary semiconductors, oxides, and ionic crystals (salts)—the phenomenon of "self-excited" emission has been observed: when the initial specimens are heated without any preliminary external influences (excitation[3]), peaks appear on the temperature curves. These effects are manifested particularly clearly when the test substances are subjected to a preliminary treatment leading to the hydration of the surface. Intense TSE is observed after metals are wetted with water[61], semiconductors are etched[37], alkali metal halides are hydrated[36,62], etc.

The initial metals[61], which did not exhibit emission, were wetted with water, dried, and heated at a linear rate in air, while recording the charges with an open counter. The "self-excited" TSE curves (t_{max} = 295°C for Al, 225°C for Fe, and 225° and 270°C for Cu) were compared with the curves obtained for the same specimen after mechanical cleaning. A satisfactory agreement of the temperatures of the peaks was observed, but the intensity of the maxima was significantly higher for the metals wetted with water. For germanium specimens subjected to mechanical treatment and wetted with water, the temperatures of the peaks varied in the range between 240° and 360°C, depending on the duration of treatment with water, i.e. the degree of hydration. It was concluded[61] that the exoemission parameters are not constants of the substance, but are determined by the method used for the preliminary treatment. The processes occurring in the oxide film are responsible for the emission. On dehydration, structural changes take place in the oxide and lead to the formation of capture levels (emission centres).

Direct experiments *in vacuo* established[30,63–65] that, when highly hydrated oxides such as Al_2O_3, MgO, synthetic zeolites, etc. are heated, the increase in TSE intensity is accompanied by vigorous gas evolution at certain temperatures (140–160°, 280°, and 360°C). Later these results were checked and confirmed[15]. Simultaneous studies of thermally stimulated emission and thermal desorption accompanied by condensation or mass-spectrometric analysis led to the conclusion that the self-excited emission is caused by the desorption of water. Calculation showed that one electron is emitted for approximately 10^6 desorbed molecules. Fig. 3 presents the results of studies on TSE and the rate of thermal desorption from magnesium oxide[64]. The present author's special experiments[50] under ultrahigh vacuum conditions (10^8–5 × 10^{-9} mmHg) showed that the observed effects are not a consequence of "parasitic" signals arising in the detector due to gas evolution, as suggested by Burkhanova et al.[15]

Bohun, who is the author of the most widely accepted theory of exoemission based on the band model[14], notes that some results do not fit within the framework of this concept. Thus distinct TSE peaks have been observed for initial alkali metal halides without colour centres in the range 230–430°C, particularly when the specimens were wetted with water, alcohol, etc.[62] It was suggested that reactions take place on the surface of the crystal coated by the adsorption film and result in the emission and desorption of both neutral and charged species. However, since the experiments were carried out in air and the emission was recorded with an open counter, the above postulates could not be subjected to an experimental test. Studies *in vacuo*, in which the emission was recorded with a secondary electron multiplier accompanied by mass-spectrometric analysis, showed[36] that the "self-excited" TSE from sodium chloride is due to the desorption of water (in the form of negative ions).

Thus it has now been established for substances of different classes—metals, semiconductors, and dielectrics—that emission occurs not only as a result of adsorption with liberation of energy but also accompanies desorption processes involving the absorption of energy. These phenomena could not be understood from the standpoint of the available hypotheses and were explained from the standpoint of the physicochemical mechanism of exoemission developed by the present author[25] (see also Section VI).

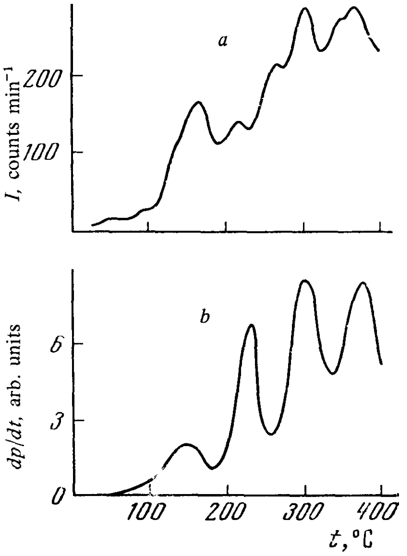


Figure 3. Temperature variation of the intensity of "self-excited" TSE (*a*) and of the rate of thermal desorption (*b*) from an MgO surface[64].

Desorption, which is an important stage in the activation of many adsorbents and catalysts, leads, according to the data examined above, to the formation of excited states with long relaxation times, which is important for the understanding of the processes involving the formation of an active surface.

3. Exoemission and Catalysis

According to modern ideas, heterogeneous-catalytic processes take place at active centres where electron exchange in the catalyst–substrate system is facilitated. Exoemission also occurs from a small fraction of the surface (active centres) where the binding of electrons is weakest; only approximately 10^{-6} of the surface atoms are capable of emission. Since such emission is observed over a wide range of temperatures, including the temperatures where heterogeneous-catalytic reactions occur (20–500°C), exoelectrons may participate in catalytic reactions. On the basis of these considerations, some workers pointed out a possible relation between emission and catalysis already in the early stages of this research[62,66]. Definite correlations were established between catalytic activity and emission capacity for substances of different classes—metals, semiconductors, and adsorption catalysts[67-69] (Fig. 4). As in studies involving the application of the majority of physical methods, catalysis and exoemission were investigated in such research under different conditions and only indirect conclusions about the causes of the observed correlations could be made.

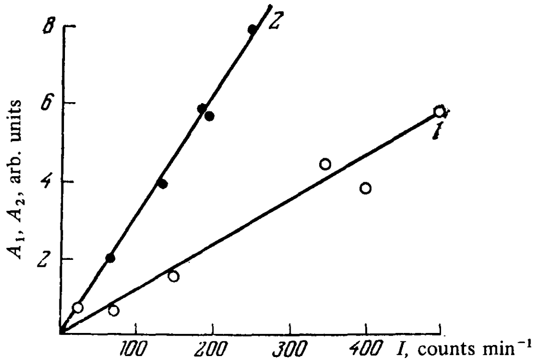


Figure 4. Relation between the emission capacity and catalytic activity: 1) $Pt(SiO_2$ with different platinum contents in the vapour-phase hydrogenation of cyclohexene[69]; 2) ZnS.Cu with different copper contents in the decomposition of methanol[68].

Studies have now been published where the heterogeneous-catalytic reactions were carried out directly in the chamber for the measurement of exoemission with simultaneous recording of the emitting charges. Exoemission from a silver catalyst in the course of the partial oxidation of ethylene has been investigated[70]. It was shown that the emission intensity in the range 150–210°C is proportional to the rate of formation of epoxyethane. At a constant temperature (250°C), non-decaying emission, accompanying the oxidation reaction, was observed. Exoemission under such conditions is regarded as thermal electron emission from a thin semiconductor oxide layer, for which the electron work function is reduced as a result of the adsorption of the epoxyethane formed. The authors support this view by the finding that exoemission is not observed during the reaction on copper, nickel(II) oxide, and iron(III) oxide, where only complete oxidation of ethylene takes place.

However, it is noteworthy that the authors[70] carried out experiments in which emission was recorded by a gas-filled counter and a component of the reaction mixture (ethylene) played simultaneously the role of the quenching gas. Under these conditions, the presence of oxygen and of water vapour (produced by the reaction) in the atmosphere of the quenching gas might have interfered with the operation of the counter and might have distorted the results of the measurements.

Another investigation[71] was undertaken to study the emission accompanying the catalytic oxidation reactions of CO, H_2, and NH_3 on a heated platinum wire. The experiments were performed *in vacuo* at partial pressures of the reacting gases of 10^{-6} mmHg. The authors attempted to discover whether exoemission is a necessary stage in the heterogeneous oxidation or whether it merely accompanies the catalytic reaction but has no influence on the latter. It was found that the increase or suppression of the emission capacity of the platinum catalyst when a negative potential is applied to it is accompanied by the simultaneous increase or decrease of the rate of catalytic oxidation. Hence it was concluded that exoelectrons are directly involved in heterogeneous-catalytic reactions. It is suggested that the observed correspondences are based on the same rate-limiting stage in both processes—the adsorption stage—which is believed[53] to be accompanied by intense emission.

However, the observed effects[71] can hardly be attributed to the involvement of exoelectrons in the reactions. This is indicated by two fundamental factors: the fairly high temperatures at which the emission and catalytic reactions take place (⩾ 800°C) and the fairly large currents (~ 10^{-8} A), which are not characteristic of exoemission. It is more likely that Richardson thermal emission from the platinum wire and the changes in its intensity owing to the increase or decrease of the thermal electron work function following the adsorption of oxygen, hydrogen, etc. are involved here.

The phenomenon of exoemission accompanying catalytic reactions in the adsorption layer at temperatures between 100° and 400°C, typical for catalytic reactions, has been observed and investigated[72,73]. A study was made of the catalytic oxidation and decomposition reactions on metals, oxide semiconductors, and ionic crystals. The experiments were formulated on the basis of the following initial postulates. The binding energy of oxygen in the surface layer of oxides is known to determine to a large extent their catalytic properties in oxidation reactions. Only "mobile" oxygen participates in reactions on specimens with inhomogeneously bound oxygen[74]. On the other hand, it has been shown that thermally stimulated emission processes are accompanied by the desorption of active gases and vapours[30,31]. Analysis of the results of comprehensive studies led to the conclusion that the emission and desorption centres are formed by mobile oxygen atoms on the surface layer of the oxide[25].

The oxidation of hydrogen and carbon monoxide has been studied[73] on oxides with hole (NiO) and electronic (ZnO) types of conductivity and on a metal (platinum black). The reaction was carried out in a cell for the measurement of exoemission with simultaneous recording of negative charges by a secondary electron multiplier. The catalyst was activated in oxygen (400°C) and hydrogen was then adsorbed. Emission, decaying with time, was observed for platinum black even at room temperature. The decay was found to be represented by the sum of two exponential functions with relaxation times τ_1 = 300 s and τ_2 = 3700 s. This was accompanied by the emission of not only electrons but also ions, the presence of which was detected by measurements in a deflecting magnetic field. Subsequent heating at a linear rate of both platinum and NiO led to the appearance of more or less distinct emission peaks at 130–150°, 180–190°, and 240–260°C. Repeated heating results in a change of the relative intensities of the peaks, which indicates the formation of active centres during the reaction (Fig. 5). The conclusion that catalytic reactions occur under the given conditions was confirmed by the results of thermal desorption analysis[73].

In conformity with the mechanism proposed by the present author[25] and later by Euler et al.[134] for exoemission from oxides, the TSE peaks are due to valence transformations in the layer of adsorbed oxygen, for example:

$$O_2\,(\text{ads.}) + e \underset{\text{stimulation}}{\overset{\text{excitation}}{\rightleftarrows}} O_2^-\,(\text{ads.})$$

The same forms of oxygen are reactive in heterogeneous-catalytic oxidation[74]:

$$O_2 \rightarrow O_2^- \text{ (ads.)} \rightarrow O^- \text{ (ads.)} \rightarrow O^{2-} \text{ (ads.)} .$$

When charged forms of oxygen interact with the substance being oxidised, there is a reverse electron transfer to the catalyst according to Boreskov[74]. It follows from the data in Fig. 5 that the electrons liberated in the catalytic step can leave the surface ("exoemission"). A possible reaction mechanism is presented below[73]:

$$O^{2-} \text{ (ads.)} + H \text{ (ads.)} \rightarrow OH^- \text{ (ads.)} + e \text{ (loc.)} + Q_{rec}, \quad (1)$$

$$O^- \text{ (ads.)} + H \text{ (ads.)} \rightarrow OH^- \text{ (ads.)} + Q_{rec}, \quad (2)$$

$$OH^- \text{ (ads.)} + H \text{ (ads.)} \rightarrow H_2O^- \text{ (ads.)} + Q_{rec.} \rightarrow H_2O^- \text{ (gas)}, \quad (3)$$

$$e \text{ (loc.)} + Q_{rec} \rightarrow e\uparrow \quad \text{etc.} \quad (4)$$

Electrons are ejected outside the limits of the crystal as a result of the recombination energy of ions and radicals[25,73]. A similar oxidation mechanism, but without allowance for electronic transitions, has been proposed by Khasin and Boreskov[75].

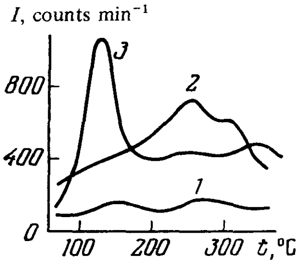


Figure 5. Thermally stimulated emission from an NiO surface: 1) before admission of reaction mixture; 2) after admission of reaction mixture (H_2–O_2); 3) after subsequent heating[73].

Analogous results were obtained in studies on the exoemission accompanying the catalytic decomposition in the adsorption layers of methanol (on Al_2O_3 and NaCl powders) and formic acid (on an NaCl single crystal).[72] It was established that the appearance of the most intense maxima at $t > 200°C$ is accompanied by the formation of decomposition products. The smaller low-temperature peaks are due to fluctuation processes in the adsorption layer (the "pre-catalytic" state). The emission of negative charges—electrons and ions—in catalytic decomposition processes in the adsorption layer is also explained from the standpoint of the radical mechanism of exoemission proposed by the present author[25]. The formation of radicals as intermediates in the catalytic decomposition of alcohols has been demonstrated experimentally[76].

It was found that the decomposition of methanol on a hydrated NaCl surface is accompanied by a shift of the most intense TSE peak to lower temperatures[77]. The products of the dissociative adsorption of water, particularly protons, can serve, by virtue of their high mobility, as energy transferring agents in surface migration and recombination processes; this in fact explains the promoting role of water. The surface diffusion of water plays a decisive role in many cases in chemisorption and catalysis[78].

4. Thermally Stimulated Emission in Phase Transformations

It was shown for the first time in 1950[1] that phase transformations are accompanied by the emission of negative charges. A sharp increase of emission was recorded in the solidification of Wood's alloy and in the allotropic transformations of chromium, selenium, etc. modifications. It was suggested that the emission is caused by exothermic processes. Later these studies were developed further[79-81]. Exoemission has been observed in the transition from the hexagonal to the cubic configuration of thallium[79], in the solidification of bismuth, cadmium, and their alloys[80], in the solidification of aqueous ammonia solutions[81], and in liquid gallium at the temperatures corresponding to structural transformations[82]. The emission was recorded with gas-filled or open counters. Studies on exoemission in phase transformations have already been reviewed in detail[83].

The authors[80-82] emphasise that the observation of exoemission from metals and alloys in their phase transformations requires photostimulation and suggest that the emission of charges is caused by deformations in the oxide film and not by its disruption.

Studies with a gas-filled counter led to the observation of the exoemission accompanying the solidification of lead (t_{max} = 235°C), tin (t_{max} = 235°C), and the lead–tin eutectic alloy (t_{max} = 180°C).[84] However, experiments showed[85] that *in vacuo* emission accompanying phase transformations is not recorded. The available data concerning the coincidence of the TSE peaks with the temperatures of allotropic transformations are also contradictory. Thus, in a study of the transformation of layers of the hexagonal modification of chromium obtained by an electrolytic method, a TSE maximum was observed at 230°C, while the phase transition temperature is 180°C. It is suggested[85] that the thermally stimulated emission is caused by oxidation processes.

In contrast to earlier investigations[84,88], peaks of exoemission from tin and lead were found[87] not only on solidification processes but also on fusion, and for bismuth the emission maximum was observed only on fusion. It was established that, in the absence of an oxide film, there is no emission and that the most intense TSE peaks are observed for an optimum thickness of the oxide layer. The authors[87] suggest that the phase transitions occurring on solidification lead to stresses in the oxide layers, which are removed by the migration of dislocations. The annihilation of dislocations carrying opposite charges leads to the release of phonons, whose energy is sufficient for the liberation of electrons from capture levels.

Despite the ambiguity of the results and of their interpretation, exoemission is recommended for the determination of phase transformation temperatures in those cases where they cannot be found by other methods, for example by thermal analysis. Rostovtsev[88] determined the limits of the solubility of zinc in aluminium (at 100–275°C), the emission being recorded with a gas-filled counter. It was established for a series of alloys of different compositions that TSE peaks correspond to the thermal decomposition temperatures of the solid solution (α) with formation of crystals (β). The results agree with data for the solubility of zinc in aluminium obtained by other methods.

The ageing processes in the aluminium–magnesium–silicon alloy have been investigated[89]. The PSE decay curve at a constant temperature shows a maximum corresponding to the segregation of the excess of the Mg_2Si phase from the supersaturated solid solution. This emission flash is shown 60 min after the start of "ageing" and occurs at the instant of segregation of Mg_2Si found by other methods (for example by electron microscopy). It was concluded that exoemission is a simple and extremely sensitive method for the investigation of the technologically important alloy ageing processes.

Studies have been made on the exoemission in second-order phase transformations[90–93]. The exoemission method has been used to investigate the γ–ϵ transformations of the manganese austenite alloy and of the first- and second-order phase transformations in iron–manganese alloys of different compositions[91,93]. The emission was recorded *in vacuo* with the aid of a secondary electron multiplier. The TSE peaks occurring on heating and cooling were attributed to first-order ($\epsilon \rightleftharpoons \gamma$) and second-order (for example, the transition from antiferromagnetic austenite to paramagnetic austenite) phase transformations. The results were explained[92] by the increased mobility of dislocations at the phase transition temperatures. It is suggested that the intensity of the TSE peaks is associated with the "degree of completion of the phase transformation and the number of structural defects"[93] and the role of physicochemical processes in oxide and adsorption films is not taken into account.

The magnetic transformations in nickel, chromium, and the oxide films coating them have been investigated[92,94,95], the emission being measured with a gas-filled counter. The TSE maxima were observed under illumination at the temperatures corresponding to the Néel points for the oxides (NiO and Cr_2O_3) covering the metal and at the Curie point of the initial nickel. It was established that the fundamental parameters—the temperatures of the peaks and the emission intensity—are determined by the thickness of the oxide layer. It was concluded that the exoemission method can be used to investigate not only phase transformations but also the gas corrosion of metals and in the solution of the problem of the formation of protective coatings in the form of thin films of metals and dielectrics.

Exoemission on heating and cooling has been observed for $Fe_{1-x}S$ pyrite specimens cut out of a lump of the mineral[96]. The peaks and inflections on the curves were attributed to the polymorphic and magnetic transformations in microregions of the crystal with a different phase composition. The powdered specimens did not exhibit emission peaks under these conditions. The exoemission method was suggested for the study of the degree of homogeneity and composition of complex minerals in those cases where the phase transition points depend strongly on the stoichiometry.

The changes in emission intensity at the phase transition points are said[95] to be caused by processes occurring on the specimen surface, for example, the generation of stresses and cracks during plastic deformations in the oxide film owing to abrupt changes in the thermal expansion coefficients. The observed emission is accounted for by the possible local decrease of the electron work function owing to the displacement of dislocations onto the surface followed by adsorption (photosorption) or heterogeneous-catalytic processes when the emitter interacts with the quenching vapour of the counter, etc.[95]

Thus the data available at the present time for exoemission in first- and second-order phase transitions in metals and alloys are contradictory. Depending on the previous history of the specimen and the state of the surface, the TSE peaks may or may not coincide with the phase transition points; the emission observed on heating the specimens, i.e. in phase transformations involving absorption of energy, is difficult to interpret.

There are two views on the nature of the emission in phase transformations. The first is based on the consideration of physical processes only. The emission peaks observed on heating certain ferroelectric substances, for example, are regarded[97] as a result of the "filling of traps with electrons and the liberation of electrical energy in phase transitions". The second view, which takes into account the role of physicochemical factors, is based on the absence of exoemission from metals and alloys lacking an oxide layer, which has been firmly established experimentally[85,87]. A detailed analysis of the available data leads to the conclusion that the emission accompanying phase transitions is caused by a set of complex physicochemical transformations in the oxide and sorption films and can be understood on the basis of the physicochemical concept described below (see Section VI).[25]

In studies of the thermally stimulated emission accompanying the decomposition of certain salts, particularly hydrated salts, it was observed that heating of hydrated quinine sulphate gave rise to an intense emission at 75–100°C; the corresponding emission peak was also observed on cooling[1]. It is suggested that these phenomena are caused by the liberation and absorption of water[1]. Later these studies were repeated[98,99]. The emission and the accompanying luminescence phenomena were absent when quinine sulphate had been dehydrated beforehand.

More detailed studies of emission from hydrated sulphates, chlorides, carbonates, etc. were made by Hanle et al.[100] The charges were recorded *in vacuo* with the aid of a secondary electron multiplier. In all the cases investigated, the liberation of the water of crystallisation was accompanied by the emission of negative ions. The number of TSE peaks corresponded exactly under these conditions to the number of singular points associated with the decomposition of hydrates of different composition; however, the TSE maxima were somewhat displaced towards higher temperatures.

Exoemission was also observed in the decomposition of certain nickel compounds[101]. Thermally stimulated emission was recorded by a gas-filled counter under illumination. The TSE peaks corresponded to the decomposition temperatures of the initial compounds, which was confirmed by X-ray diffraction analysis. Repeated heating led to the observation for all the compounds of the same maximum at 230°C, which was attributed to a phase transition in nickel(II) oxide (the Néel point). The author[101] notes that the method described makes it possible to investigate the kinetics of the thermal decomposition of chemical compounds and to analyse the decomposition products.

IV. EXOEMISSION AND MECHANOCHEMISTRY

1. Metals

For metals, exoemission caused by mechanical influences is in fact of greatest interest. This is because of the possibility of employing exoemission in the study of deformations, the processes involved in the mechanical treatment of machine components, the fatigue resistance of materials, etc. Studies in this field have been concerned with the emission caused by plastic and other deformations, friction, milling, sand-blasting, etc.[1,26,48, 58,59,102]. In these excitation methods, dislocations and point defects (vacancies) and their diffusion and annihilation play a significant role. Secondary surface processes take place simultaneously—the disruption of the oxide film and desorption as well as adsorption and oxidation, these being largely caused by the migration of dislocations onto the surface.

On the other hand, the influence of the physical chemistry of the surface on the mechanical (plastic) properties of metals has been vigorously investigated recently. Deformations are known to be facilitated by adsorption, the effect having been explained by Likhtman et al.[103] The significant influence of oxide and other special coatings on the mechanical properties of metals has been demonstrated. Oxide and other surface formations lead to the generation of energy barriers, preventing the emergence of dislocations; the decrease of the height of these barriers on polishing, etching, and the adsorption of surfactants facilitates deformation.

There is experimental evidence showing also that adsorption processes are the cause of deformations in the surface layer: depending on the nature of the adsorbent-adsorbate system and on the degree of surface coverage, both expansion and contraction can take place[104]. It follows from the foregoing that exoemission, deformation, and adsorption (desorption) phenomena are indissolubly linked and that they should be considered simultaneously.

There exist at present two fundamental and in a certain sense contradictory views on the nature of exoemission from deformed metals. Some investigators[105-108] believe that the processes determining emission occur in oxide layers, while others[57-59] claim that the emission kinetics are determined by the diffusion of defects (dislocations, vacancies) and that emission occurs as a result of the decrease of the electron work function caused by deformations.

A quantitative correspondence between the degree of deformation and the intensity of exoemission has been found[105,106]. The following emission mechanism has been proposed[106]. Plastic deformations lead to the generation of mobile point defects (vacancies) which migrate towards the surface and form capture layers in the forbidden gap of the oxide. The defects produced behave as centres of photoemission and thermally stimulated emission. The significant role of the formation and migration of vacancies and dislocations has been emphasised also in other investigations[57-59,107-109]. It has been shown that the emission intensity $I \propto \epsilon^n$, where n is the degree of deformation. After carrying out experiments on emission from deformed aluminium coated by oxide films of different thickness, Sujak[107] concluded that the emission takes place from charged cracks in the oxide. This model is analogous to that proposed previously[110]. It has been shown[111] that the intensity of emission on deformation increases significantly in the presence of moisture in the atmosphere of the quenching gases of the counter. It is suggested that moisture neutralises the strong electric field arising across the cracks, which hinders the release of electrons. Results obtained with a Geiger counter were confirmed by experiments *in vacuo* using a secondary electron multiplier as the recording instrument[112].

In other studies[57-59], it was suggested that exoemission is determined by the proportion of defects and by the nature of the elementary deformation steps, which depend on the nature of the metal itself. The authors believe that the "deformation excitation" possesses definite specific features and that the emission of electrons accompanying it should be regarded as an independent type of emission. There are numerous experimental facts indicating the lack of validity of these claims. It is also difficult to justify theoretically the existence in a conducting metal of trapping levels giving rise to the prolonged relaxation times of the excited states responsible for exoemission[48,114]. For example, it has been shown[25,48] that exoemission parameters are independent of the method of excitation. On deformation, the emission intensity always increases to a certain limit, after which it falls exponentially (Fig. 1). A similar type of curve with a maximum occurs when an atomically clean metal surface is exposed to active gases[49] and is explained by adsorption and oxidation phenomena. In support of their view that the exoemission on deformation is caused exclusively by the formation of structural defects, the authors[113] present the results of experiments in an ultrahigh vacuum, where PSE was observed following the extension of an aluminium specimen and attribute fundamental importance to them. No account was taken of the fact that, under the conditions of treatment adopted (degassing at 400° C), an atomically clean surface is not obtained and that the observed emission is caused by the degradation of the oxide layer. It has been shown[48,56] that, in the case of an atomically clean surface, mechanical treatment under the conditions of an ultrahigh vacuum does not lead to the occurrence of either photoemission or thermally stimulated emission.

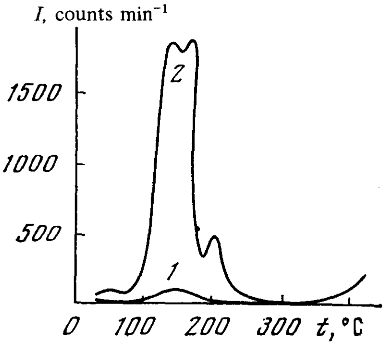


Figure 6. Thermally stimulated emission from a quartz specimen after vibromilling *in vacuo* (curve *1*) and in an atmosphere of oxygen (curve *2*).[125]

Depending on the thickness of the oxide layer, either PSE, which depends on the pressure of the residual gas (layer thickness $d \leqslant 45$ nm), or dark emission ($45 \leqslant d \leqslant 230$ nm) is observed on deformation by extension[114]. In the former case, PSE is analogous to that observed when the surface is cleaned[56] and is caused by the decrease of the electron work function owing to the adsorption of water. In the latter case exoemission is due to the disruption of the oxide film and occurs without photostimulation.

In calculations on the kinetics of exoemission from deformed metals, the authors[115,116] also took into account the cracking of the oxide film, the diffusion of vacancies to the surface, and the interaction of the freshly formed surface with the gases in the surrounding medium followed by oxidation, in contrast to earlier views[57-59].

Exoemission on friction has been examined in detail by Evdokimov and Semov[102], who investigated emission under dynamic conditions during friction and after its cessation, in the absence and presence of lubricating materials. The photostimulated emission was recorded by an open counter in air. For different types of steel and cast iron, the PSE intensity after the cessation of friction passed through a maximum; for the chemically more reactive aluminium, emission whose intensity diminished exponentially was observed. These findings are analogous to those obtained on deformation[57,58] and on adsorption of active gases on freshly formed surfaces[48,56].

Thus the kinetics of exoemission on deformation of metals, friction, and adsorption of gases on freshly formed surfaces are determined by the physicochemical transformations which accompany the relaxation processes in a damaged surface layer.

2. Non-Metallic Crystals

For non-metallic crystals, emission decaying over a period of time has been observed after comminution and grinding[1]. Numerous minerals and inorganic and organic crystals have been investigated. It has been noted[1] that, on comminution *in vacuo*, the crystals acquire an appreciable charge, which plays a significant role in the observed effects. The formation of charges accompanying emission on heating single crystals (LiF) was recently confirmed by direct measurements[117]. The density of the elementary charges was 10^{10} cm^{-2}, but the charging mechanism is not clear. One of the possible explanations is based on the model involving the formation of a "triboplasma", arising when the crystal is cleaved. High energy levels of the emitted electrons were observed; the greatest number of electrons had an energy of 20 keV, while the maximum observed energy was approximately 120 keV. The field strength calculated from the formula $E = \sigma/\epsilon_0$ proved to be approximately 10^5 V cm^{-1}, so that the observed emission is not cold ("field") emission.

Independently of Kramer's study[1], the phenomena of the emission of negative charges in processes involving the dissociation of adhesion and cohesion linkages were investigated and described by Krotova[118], who observed the emission of fast electrons with energies of several keV. It was suggested that the high energies are caused by the acceleration of electrons in the strong fields of the electrical double layer arising following the breakdown of contacts. The phenomenon was called "mechanoemission". The mechanism of these processes is probably different from that of the exoemission of slow electrons. However, it must be emphasised that the after effects, consisting in the relaxation of the excited states arising following the breakdown of adhesion and cohesion contacts, are exoemission. This is indicated by the emission kinetics, which are the same as those observed after excitation by other methods, the low electron energies, and a number of other factors.

The significant role of dislocations in exoemission from ionic crystals has been noted. It has been established[119] that, when LiF is cleaved, mobile dislocations with a free path of several centimetres are formed. The hypothesis has been put forward that these dislocations transport the excitation energy generated by electron bombardment. The intensity of thermally stimulated emission from LiF caused by irradiation with X-rays increases with increase of the density of dislocations[120]. According to Knab and Urusovskaya[120], the observed effect is a consequence of the increase of the number of point defects owing to the interaction of dislocations. The thermal stability of the *F*-centres (the position of the TSE peak) is determined by the interaction of the point defects with dislocations of different types[121]. The authors do not take into account the possible processes involving radiation-induced and postradiation adsorption following the excitation of specimens in air and the recording of the emission by a counter. The conclusion concerning the lack of influence of adsorption layers on exoemission from deformed LiF crystals, reached in some investigations[122,123], are insufficiently justified, since the authors did not undertake special cleaning of the surface, although they recorded the emission under ultrahigh vacuum conditions.

It has been shown[124] that the cleavage of alkali metal halide crystals is accompanied by appreciable gas evolution. It was found that the structural defects generated by the vibromilling of quartz are capable of emission only in the presence of adsorbed oxygen (Fig. 6).[125] Under these conditions, the TSE peak ($t_{\max} \simeq 150°$C) coincides with the maximum in the rate of desorption of oxygen from such oxides[126].

A detailed analysis of data for exoemission caused by mechanical influences on metals and non-metallic crystals leads to the conclusion that the presence of adsorption layers plays a decisive role under these conditions.

V. EXOEMISSION AFTER EXCITATION BY IONISING RADIATION

1. Metals, Semiconductors, and Oxides

Like mechanical treatment, ionising radiation does not excite exoemission from the atomically clean surfaces of metals and semiconductors[45,48]. It is therefore useful to examine emission only from real metals and semiconductors coated by an oxide layer. It has been established[127-129] that, independently of the nature of the metal, the thermally stimulated emission peaks occurring after excitation by X-rays are located in the same temperature ranges (140-160° and 260-280°C). The same peaks have been observed for aluminium[48] acted upon in other ways: milling and exposure to β-radiation. It was concluded that exoemission is excited from the capture levels in the oxide layer.

It has been established for the majority of powdered oxides, excited by electron bombardment, that the TSE peaks are located in the same temperature ranges as for metals[30,127] (Fig. 7). The number and relative intensities of the peaks are independent of the nature of the oxide (semiconductors with electron or hole conductivity as well as insulators), but are not determined by its previous history. The emission capacity of the oxide can be significantly reduced by vacuum heat treatment and increased as a result of the adsorption of active gases and vapours.

It has been established[130] that, following the adsorption of electron-donating gases (hydrogen), the emission capacity of Al_2O_3 excited by X-rays increases, while, on treatment with electron-accepting gases (N_2O, CO_2), it falls. It is suggested[131] that hydrogen adsorbed in the atomic form generates shallow donor levels and that hydrogen and deuterium atoms lead to the formation of donor levels of different depths (the "isotope effect").

The authors of the above investigations begin their interpretation with the concepts of the band model of exoemission and the electronic theory of chemisorption, assuming that the molecules (atoms) of the adsorbed gases generate donor (acceptor) levels, increasing (decreasing) the concentration of the conductivity electrons responsible for exoemission.

More detailed studies for more oxides showed that, in contrast to electrical conductivity, the emission capacity is not determined by the electron-donating or electron-accepting nature of the adsorbed molecules (atoms): the adsorption of oxygen, a typical electron acceptor, on the surfaces of silicon, ZnO, ZnS, SiO_2,[25,37,132,133] and BeO[134] leads to an increase of emission capacity. The band model, which takes into account the role of the concentration of conductivity electrons and of the surface potential in exoemission, cannot explain these results. It is suggested that thermally stimulated emission takes place directly from the capture levels generated by different forms of adsorbed oxygen[30,133,134].

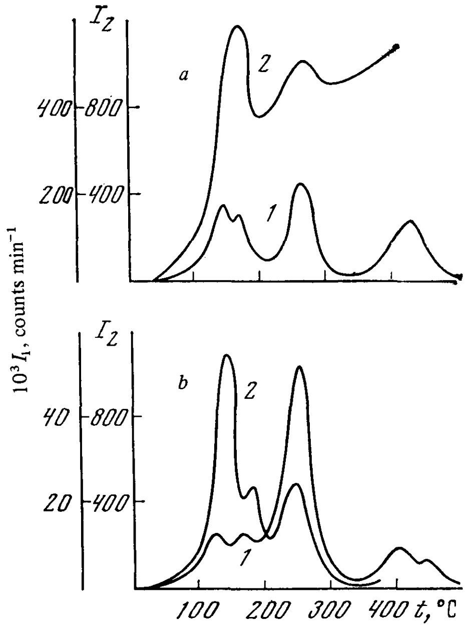


Figure 7. Thermally stimulated emission after excitation by electron bombardment: *a*) from aluminium[129] (curve *1*) and corundum[30] (curve *2*) surfaces; *b*) from nickel[129] (curve *1*) and nickel(II) oxide[73] (curve *2*) surfaces.

It has been established in a recently published study[132] that the surface states responsible for exoemission from oxidised silicon excited by low-energy electrons are generated by adsorbed oxygen (O_2^-). The physical model of the excitation and emission of exoelectrons is based on the potential curves for the excited state of the negatively charged form of adsorbed oxygen. It is concluded that the TSE method can yield valuable information about the state of the adsorbed molecules. This is of interest for both fundamental and applied research, particularly in the field of heterogeneous catalysis.

2. Ionic Crystals

For ionic crystals (crystalline phosphors and alkali metal halides), the commonest method of excitation is treatment with ionising radiation. The electronic energy level schemes for crystalline phosphors and coloured alkali metal halides have been deduced theoretically and investigated experimentally in considerable detail. An analogy has been found between exoemission and luminescence phenomena[1,9–11], which has in fact served as a basis for the development of the most widely accepted band model of exoemission. Like luminescence, exoemission can be excited by short-wavelength light and by high energy radiation (electronic and ionic bombardment, by X-irradiation and β-irradiation, by exposure to a glow discharge, etc.). After the removal of excitation, the decay of the afteremission and the afterglow are described by the same laws. Heat treatment frequently leads to the appearance of TSE peaks and thermoluminescence in the same temperature ranges. It is believed[11] that the analogy is based on common elementary physical processes. At the same time there are also differences between luminescence (bulk-phase effects) and exoemission (a surface phenomenon) phenomena. Luminescence is associated with the presence of activator atoms, while, according to the band scheme, exoemission should be independent of their presence.

Results which do not fit within the framework of the proposed model have been published. For example, it has been found that the intensity of the afteremission excited by electron bombardment depends on the activator concentrations[52]. Agreement between the numbers and temperatures of the exoemission and luminescence peaks is not always observed. The discrepancies between the results of different workers and the marked dependence of the thermally stimulated emission spectra on the technology of the preparation of the phosphors[135] led to the conclusion that surface states are involved in these phenomena; however, the nature of these states has not been considered.

The main objects of the fundamental investigations of exoemission and luminescence are sulphides, sulphates, and alkali metal halides. A correlation between the temperatures of the PSE and thermoluminescence peaks has not been observed for sulphides[136,137]. On the basis of the results of studies *in vacuo*, Behmenburg[136] suggested that in the case of zinc sulphide thermoluminescence is caused by the presence of capture levels in the crystal, while thermally stimulated emission takes place from trapping levels in the adsorption layer (for example, of oxygen). However, the nature of this layer was not investigated.

Exoemission from activated sulphides has been studied[67,138,139] using both a gas-filled counter and a secondary electron multiplier *in vacuo* as recording instruments. In the former case, it was found that the activator (Cu, Ag) has a significant influence on the absolute and relative intensities of the TSE peaks[67,138]. The observed direct relation between exoemission and catalytic activity permitted the conclusion that the emission centres (activator ions) are either the centres of the activated adsorption of methanol or the catalytic centres.

After electron bombardment, TSE peaks were observed for ZnS.Cu, ZnS.Ag, and ZnS.Al single crystals[139] in the same temperature ranges: at 120–140°, 160–180°, and 220°C. Vacuum heat treatment and heat treatment in hydrogen reduced significantly the emission intensity, while the adsorption of oxygen, water vapour, and methanol increased it. The adsorption of an electron-donating gas is known to increase the concentration of conductivity electrons in a semiconductor and to reduce the surface potential, while the adsorption of oxygen acts in the opposite direction. These findings lead to the conclusion that, in contrast to the hypothesis of the band model, the exoemission from the sulphide surface takes place without the participation of the conductivity electrons and that the emission parameters are not influenced by the surface potential either.

Thermally stimulated emission from sulphates has been studied[1,9,11,135]. The emission intensity was measured using as recording instruments a counter after excitation with X-rays or a secondary electron multiplier *in vacuo* after excitation by electron bombardment. Data concerning the positions of the TSE peaks and their correlation with thermoluminescence (TL) are contradictory; the involvement of the activator in the formation of the electron localisation levels on the surface of sulphates is likewise controversial. These contradictions are associated with the differences in the technology of the preparation of the specimens[135], in the methods and duration of their storage[140], and in the methods of excitation and recording which have a significant influence on the state of the adsorption layers. Depending on its previous history, the temperatures of the TSE and thermoluminescence peaks for the same specimen can both coincide and diverge[141].

A correlation between the thermally stimulated emission and thermoluminescence phenomena is observed when gas and vapour molecules adsorbed during technological treatment, during excitation of the emission (radiation-induced adsorption), or during recording (postradiation adsorption of the quenching vapour of the counter) are involved in these processes. Luminescence is a bulk-phase phenomenon and the role of adsorbed gases is not usually considered in this connection, although in dispersed systems it can be considerable. Studies where it has been shown that the luminescence of a crystalline phosphor is stimulated as a result of adsorption, particularly of oxygen and water vapour, have been published only recently. The investigations of the comparatively new phenomena of adsorbo-[142] and radicalo-luminescence[143] are noteworthy.

The exoemission from alkali metal halides coloured by ionising radiation has been the subject of detailed research[19]. It is suggested that the TSE maxima correspond to the thermal decomposition of definite colour centres regardless of the method of their generation (additive electrolytic and photochemical colour generation). For example, the TSE peak for NaCl at 110°C has been explained by the thermal decomposition of the *M*-centres and that at 280–290°C by the decomposition of the *F*-centres. A detailed analysis of the available data has shown, however, that, for alkali metal halides too, the technology of the preparation, the method and duration of the storage of the specimen, and the method of excitation and recording (gas-filled counter, secondary electron multiplier *in vacuo*) play a much more significant role in the TSE phenomena than the presence of particular colour centres and the nature and concentration of activators.

It has been established[36] that the intensity of the fundamental peaks of the TSE from NaCl, which have been attributed to the thermal ionisation of colour centres, decreases appreciably as a result of vacuum heat treatment (at 400°C) and is restored after hydration of the specimens. The adsorption of active gases and vapours (hydrogen, carbon monoxide, oxygen, and water and alcohol vapours) on the NaCl surface excited by electron bombardment causes a marked activation of exoemission[144].

It follows from the foregoing that the defects arising under the influence of ionising radiation on alkali metal halides (colour centres) give rise to emission centres only in the presence of adsorption layers.

3. Principles of Exoemission Dosimetry

The proportionality between the emission intensity and the dose of the exciting radiation was established for the first time in 1957 for calcium sulphate[145]. The introduction of an activator (manganese) makes it possible to determine very low radiation doses (0.1 mrad). The first exoemission dosimeters, based on the recording of both photostimulated[146] and thermally stimulated emission[147], were developed using calcium sulphate. The following fundamental advantages of exoemission dosimetry have been noted: the possibility of wide variation of the emitting materials, their low cost, the lack of their sensitivity to light before exposure to the action of ionising radiation, the simple technology of their treatment, the possibility of their repeated employment, and their high sensitivity to the action of low-energy radiation.

Further studies on the scope of exoemission dosimeters and their commercial production were continued in 1966–1970. Sulphates, alkali metal halides, and particularly beryllium oxide, both in the initial state and activated by the addition of metals, have been used as the materials for the preparation of the dosimeters. The number of such studies has greatly increased in the last 3 years. TSE dosimeters based on BeO have been developed in the USA for specific applications and have undergone prolonged field tests[148]. These dosimeters have definite advantages over those usually adopted (for example, luminescence dosimeters) for the accurate measurement of small doses of low-energy radiation, particularly in mixed radiation fields. A detailed review of the problem of exoemission dosimetry has been published[149]. The main unsolved problems, preventing the commercial production of exoemission dosimeters, is the stability and reproducibility of readings. It has been found that the emission parameters (the number, temperatures, and intensities of the peaks) depend significantly on the technology of the preparation and methods of storage of the dosimeters[148].

The parameters of the thermally stimulated emission from $CaSO_4$ specimens, used as a basis for the development of TSE dosimeters in the USSR, have been investigated[141]. The "ageing" effect has been observed and investigated for the activated sulphates. Thus high-temperature emission peaks are characteristic of the initial $CaSO_4$ prepared by fusion; after prolonged storage in air, the "population" of the capture levels changes—the low-temperature peak (140–160°C), characteristic of all the metals and oxides investigated, predominates. Experiments on the influence of adsorption on the TSE spectrum showed that the "ageing" effect is a consequence of the adsorption of water.

Thus the problems of the stability of the operation of highly sensitive and promising exoemission dosimeters can be solved only by detailed investigation of the physical chemistry of the surface under storage and operating conditions.

VI. THE PHYSICOCHEMICAL NATURE OF EXOEMISSION

A phenomenological theory, permitting a description and an examination of exoemission from metals, semiconductors, and dielectrics from a single standpoint, has been proposed[25]. As shown in Section I of this review, exoemission occurs as a result of the relaxation processes of the excited states and the study of its mechanism involves the analysis of the kinetic parameters—the quenching constants of the afteremission at a constant temperature and the activation energy and pre-exponential factors in the recording of thermally stimulated emission. A formal kinetic treatment of the emission processes and a mathematical model based on general physical considerations taking into account the band theory of solids have been described in a detailed review of these problems[15]. On the basis of the chemical aspects dealt with in the above review, we shall consider in this section the physicochemical picture of the exoemission phenomenon.

The emission of charges is the result of a complex set of physical and physicochemical processes in the damaged surface layer. Here the fundamental parameters are determined by the slowest stage of the reactions taking place. The coincidence of the TSE peaks for substances of different classes shows that the rate-limiting stage occurs in the surface layer whose nature is independent of the "support", for example it can be a layer of adsorbed oxygen[30,133,134].

The present author[25] believes that these layers are mobile ("quasi-insulated" from the support). In this case, the temperature of the peak, which in the general case determines the activation energy[15] of the emission processes, should depend only slightly on the nature of the adsorbent, which has been observed experimentally[25]. The mobile layer can be formed in the surface phase as a result of the adsorption of gases and vapours from the residual atmosphere *in vacuo* on excitation or heat treatment of the specimen, as suggested by Maenhout-Van der Vorst and Demuer[133], or on degradation of the oxide (adsorption) film present on the surface[150,151]. Hence it follows that the pressure and composition of the surrounding atmosphere during excitation and recording are of fundamental importance for the solution of the problem of the emission mechanism.

The fundamental emission parameters for metals, oxides, and ionic crystals (crystalline phosphors) have been compared using a counter (argon–alcohol atmosphere) as the recording instrument *in vacuo* (10^{-5} mmHg) with a residual air atmosphere and in an ultrahigh vacuum (10^{-8}–5×10^{-9} mmHg) with a residual hydrogen atmosphere[25,151]. It was found that for metals the fundamental parameters (the quenching kinetics and the positions of the TSE peaks) are independent of the method of recording, whereas for ionic crystals (phosphors) a significant discrepancy between the results is observed. This is associated with the possibility of the formation of stable radiation-induced defects in ionic crystals, stimulating the radiation-induced adsorption of gases from the surrounding medium, including the quenching gases of the counter. Experimental evidence in support of this phenomenon has been obtained in studies[139,144,152,153] where it has been shown that the radiation-induced adsorption of active gases and vapours has a significant influence on the number, temperatures, and intensities of the TSE peaks.

For excitation and recording *in vacuo*, the spectrum of the trapping levels characterised by the thermally stimulated emission is independent of the pressure and composition of the residual gases in the vacuum (air, $p \simeq 10^{-5}$ mmHg; hydrogen, $p \leq 10^{-8}$ mmHg) and of the presence of the lubricant vapour[151]. This implies that the "mobile" adsorption layer, responsible for the exoemission processes, is formed as a result of the degradation of the surface layer of the emitter on excitation.

It was shown above that exoemission takes place as a result of mechanical treatment, the action of ionising radiation, phase transformations, adsorption, desorption, and catalysis in adsorption layers. Fig. 8 presents the results of the study of TSE after exposure to different influences. The temperatures of the peaks are the same, so that the rate-limiting stage in the emission kinetics is determined by the same elementary processes regardless of the method used to generate the excited states. When mechanical influences are employed, the role of the formation of dislocations and vacancies as well as their diffusion and emergence on the surface is significant. Secondary processes take place at the same time—the disruption of the oxide film, adsorption, and oxidation, which take place primarily at the sites where dislocations and other defects emerge on the surface. Phase transitions are also coupled with the rearrangement of the structure, accompanied by the formation and degradation of the oxide layer; under these conditions, the mobility of the defects and the probability of their emergence on the surface increases and the adsorption and oxidation are activated. The adsorption and desorption processes are in their turn the cause of the deformations in the surface layer[104].

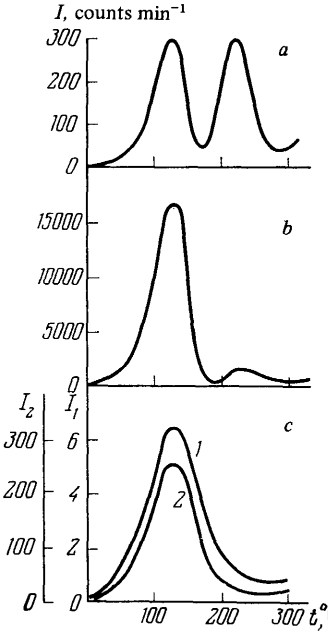


Figure 8. Thermally stimulated emission from a silicon single crystal: *a*) "self-excited" emission after etching[37]; *b*) after electron bombardment; *c*) after treatment with emery (curve *1*) and after polishing combined with exposure to X-rays[57] (curve *2*).

In constructing both the physical and the physicochemical model of exoemission, one of the central problems is the origin of the energy necessary for the release of electrons. The present author[25], who devised the physicochemical concept, believes that the source of this energy is the recombination reactions of the active species (ions and radicals) in the damaged surface layer of the solid. In a recently published study[154], it was demonstrated by direct experiments that the recombination reactions of atomic hydrogen and oxygen on the surface of the solid (for example, activated sulphates) result in the emission of negative charges (electrons and ions). On subsequent heating, thermally stimulated emission is observed. This phenomenon has been called[154] "radicalo-recombination emission".

The formation of active species (radicals, radical-ions) is possible for all the methods of excitation of the solid described above, giving rise to exoemission. Mechanical, radiation, and other influences as well as phase transformations are known to lead to the same effects—the rearrangement of the structure and ultimately the dissociation of chemical bonds and the formation of free radicals (radical-ions) together with structural defects. It has now been established by electron spin resonance that radicals are formed under radiation-induced mechanical influences during adsorption and catalysis in the adsorption layer. Mass-spectrometric studies of gas evolution from the surface of oxides have shown that electron bombardment—one of the common methods of exciting emission—causes the degradation of the hydrate coating with formation of hydrogen and oxygen[150,151].

Data illustrating the physicochemical mechanism of exoemission, based on the above reactions in the surface layer, have been published[25,30,155]. Thermally stimulated emission is a result of the following set of processes: heat treatment, phase transformations in adsorbed surface compounds (for example hydrates), the formation of a mobile adsorption layer, desorption, the generation of stresses, the relaxation of stresses (deformations in the surface layer) and electron emission (the acquisition of a positive charge by the surface). The desorption step is preceded by surface migration (de Boer's migrating or "jumping" molecules)[156]. The recombination of ions, radicals, and other active species results in two-dimensional condensation. The recombination energy is consumed in the liberation of the electrons localised on the surface. The trapping levels can be produced either by surface defects such as colour centres or by adsorbed ions (O_2^-, O^-, OH^-, etc.). The active species are recombined near specific sites (defects), energetically insulated from the lattice, where the liberated energy is not dissipated in the form of phonons, but is consumed in the excitation of electrons. The probability of triple collisions (two active species colliding with a lattice defect) is low, and this accounts for the extremely low emission currents (10^{-17}–10^{-19} A). At the excitation temperature, only part of the radicals (ions) formed recombine—afteremission and gas evolution are observed. Subsequent heat treatment leads to the stepwise recombination of the active species—thermally stimulated emission and the accompanying thermal desorption take place. The experimental evidence for the simultaneous occurrence of the thermally stimulated emission and thermal desorption processes, thermally stimulated emission and catalysis in the adsorption layer, as well as examples of reactions illustrating the physicochemical mechanism of the exoemission phenomena described above (the "chemical mechanism of the processes") are described in Section III of the present review.

Thus, according to the concepts developed by the present author[25], exoemission is a consequence of the stepwise recombination of active species in the mobile adsorption layer arising during the excitation processes. The thermally stimulated emission peaks are caused by the valence transformations in the layer of adsorbed oxygen[132].

VII. THE PROSPECTS FOR THE APPLICATION OF EXOEMISSION IN SCIENTIFIC RESEARCH AND IN ENGINEERING

The above review of the phenomena accompanied by the low-temperature emission of negative charges shows that exoemission can serve as an extremely sensitive indicator of physicochemical processes in the surface layers of solids: adsorption, desorption, oxidation, corrosion, heterogeneous-catalytic reactions, etc. Studies have shown that thermally stimulated emission makes it possible to follow the formation of the active surfaces of catalysts and adsorbents during preliminary treatment (for example, dehydration) and their activation processes, to investigate the action of the individual components of the reaction and the reaction mixture on the "energy relief" of the surface, etc.[73]

Studies on TSE during catalysis permit conclusions concerning the mechanisms of certain reactions in both the adsorption layer[72,73] and in the gas phase[70,71]. A direct relation between catalytic activity and emission capacity has been established for certain deposited and promoted systems[67,69], so that the emission intensity can serve as the basis of a method for estimating the activities of catalysts, particularly when they are poisoned by admixtures in the starting material[157].

Since exoemission is extremely sensitive to radiation, the TSE method can be used to investigate the radiation-induced damage in semiconductors and dielectrics[37,158], the phenomena of radiation-induced adsorption and catalysis[159], and heterogeneous radiolysis[159]. A relation has been established between the exoemission parameters, the proportion of defects, and the "radiation stability"[157] of materials used as the elements of lasers. The author recommends the exoemission method for the quality control of the surfaces of the elements of solid-state lasers.

The adsorption layers formed during the technological treatment of the components and their storage or operation are known to determine in many instances the reliability of the apparatus in the electrovacuum industry and in semiconductor engineering. Exoemission, which is extremely sensitive to the presence of adsorption films, particularly those of water and oxygen, can serve as an effective method for the control of technological processing in many industries[37,160].

The "ageing" effects on active surfaces, for example those of catalysts, exoemission dosimeters, and crystalline phosphors, etc. are also associated with the formation of adsorption layers. The exoemission method makes it possible to follow the changes in the state of the surface during the storage of such systems exhibiting adsorption activity[140].

Exoemission was already suggested in the initial stage of research[26] for monitoring certain technical processes involving the treatment of metals, plastic deformations, etc. This applies particularly to processes employing lubricating materials, i.e. where the structure and mechanical properties of the surface of metals play an important role. For example, exoemission from the surface of a bearing under the conditions of prolonged working of a Mercedes-Benz goods truck has been investigated[1]. A study has been made of exoemission during the deformation of technically important materials and friction[58,59,102]. It was noted above that thermally stimulated emission is also recommended for the study of first- and second-order phase transformations in metals and alloys.

Exoemission has proved to be an effective method for the investigation of comminution and sintering processes (for example in the paint and varnish industry and in powder metallurgy[26]). There is evidence for the possibility of employing exoemission in "photography"[1]. Exoemission microscopes, permitting a detailed study of the defect structures of metallic and non-metallic surfaces after mechanical, radiation, and other treatments, have been developed recently in the USA[35]. Exoemission microscopy has many advantages over electronic, thermionic, etc. microscopy. It makes it possible to reduce appreciably the temperature of the test specimens and to eliminate the activation of the surface (for example by barium, strontium, and caesium) necessary in thermionic emission from metals, and permits the investigation of semiconductors with a wide forbidden gap as well as insulators.

The likely usefulness of exoemission in biological research has been claimed recently[161]. There are publications concerning the thermally stimulated emission from certain aminoacids[162], kidney stone[163], etc. On the basis of the results obtained, the authors recommend exoemission for research in medicine and pharmacology. Mention should also be made of attempts to employ exoemission in radiological studies connected with the development of highly sensitive exoemission dosimeters for specific applications[149]. Exoemission from bone tissue, dental enamel, collagen, etc. after exposure to radioactive emission has been investigated[164].

Studies of heterogeneous-catalytic reactions have shown that oxidation processes are accompanied by spontaneous emission, particularly when they occur with proton or electron transfer. Presumably exoemission will serve as an effective method for the investigation of biochemical reactions, especially in the solution of problems such as those of photosynthesis and cell bioenergetics. These reactions are also known to include stages accompanied by the transfer of both electrons and protons.

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The above review of the results and their analysis have shown that exoemission is a complex physicochemical phenomenon and that the elucidation of its detailed mechanism is closely related to the problem of the physics and physical chemistry of the surface. Despite the fact that approximately 25 years have elapsed since the first studies by Kramer in this field, exoemission continues to be a relatively little investigated phenomenon, whose study is the concern of only a few scientists—physicists and metallurgists. However, it is known that the solution of the problems of chemisorption, catalysis, adhesion, mechanochemistry, surface phenomena in semiconductors, and the physics of thin films is closely related to the problem of exoemission and requires the joint efforts of physicists and chemists[164].

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Catalytic Oxidation of Ammonia

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Data on the catalytic properties of various substances (metals, their alloys, simple and complex oxides, and zeolites containing metal cations) in the oxidation of ammonia are described systematically and reviewed. The kinetics and mechanism of the reaction are discussed and the factors determining the activity and selectivity of the catalysts are identified. Fundamental relations between the physicochemical and catalytic properties of substances of different types are formulated and the relations between the oxidation of ammonia and the selective oxidation reactions of organic substances are analysed.

The bibliography includes 61 references.

CONTENTS

I. INTRODUCTION

The catalytic oxidation of ammonia is one of the most interesting and important heterogeneous catalytic processes. It can proceed in the following three principal ways:

$$2NH_3+1\frac{1}{2}O_2=N_2+3H_2O+151\ \text{kcal}, \quad (I)$$

$$2NH_3+2O_2=N_2O+3H_2O+132\ \text{kcal}, \quad (II)$$

$$2NH_3+2\frac{1}{2}O_2=2NO+3H_2O+108\ \text{kcal}. \quad (III)$$

In the presence of many catalysts, all three nitrogen-containing products (N_2, N_2O, and NO) are formed simultaneously at 400-500°C in various proportions. On the other hand, in the presence of selective catalysts and when the process is carried out under specific conditions (mainly at specific temperatures), one of the reactions (I)-(III) takes place preferentially. In the presence of platinum or cobalt oxide catalysts at 750-900°C, the main product is nitric oxide. The oxidation of ammonia in the presence of platinum catalysts (they usually consist of platinum-rhodium or platinum-rhodium-palladium alloy gauze) constitutes the basis of the modern industrial manufacture of nitric acid[1]. In the presence of manganese oxide catalysts at lower temperatures (300-400°C), nitrous oxide is formed in fairly high yields[2]; this product is a valuable anaesthetic used in medicine. In the presence of vanadium pentoxide at 500-600°C, ammonia is oxidised only to molecular nitrogen, the process being of practical interest for aviation[3]. Thus each of reactions (I)-(III) is of practical value.

The catalysts of these reactions described above have been discovered empirically. The improvement of the existing catalysts for the oxidation of ammonia and the search for new, more reactive catalysts require the development of scientific principles of the selection of catalysts for this process. This necessitates a systematic arrangement and classification of the available experimental data, a detailed study of the reaction mechanism, and a study of the relation between the catalystic and physicochemical properties of substances.

Very many studies have been made on the catalytic oxidation of ammonia[1,2]. Most of them concern the reaction in the presence of industrial platinum (and certain oxide) catalysts for the synthesis of NO operating at high temperatures under diffusional conditions. The main feature of this review, which distinguishes it from other surveys dealing with the catalytic oxidation of ammonia, is that attention is concentrated on the experimentally proved detailed mechanism and chemical kinetics of the reaction and also on the problem of the relation between the catalytic and physicochemical properties of the relevant substances. These problems were hardly considered in previous studies because the principal experimental and theoretical investigations on these lines have been carried out only in recent years.

The elucidation of the characteristics of the catalytic oxidation of ammonia is important not only from the standpoint of the practical selection of process catalysts but is also of general theoretical interest for the solution of fundamental problems of oxidative heterogeneous catalysis.

The reaction occupies in some respects an exceptional position among other oxidative processes. On the one hand, it has much in common with the oxidation reactions of other inorganic substances (hydrogen, carbon monoxide, etc.) for which the problem of the prediction of catalytic activity is of primary significance. On the other hand, in the oxidation of ammonia there arises the problem of the selectivity of catalytic action, which makes this process similar to many oxidation reactions of organic substances.

In organic catalysis, it is usual to distinguish the products of mild and extensive oxidation. The latter are characterised by a relatively high atomic fraction of oxygen. In the series of ammonia oxidation products N_2-N_2O-NO, the atomic fraction of oxygen rises from zero to 1/2. The degree of oxidation of nitrogen and the number of O_2 molecules required to oxidise one NH_3 molecule increase in the same sequence [see reactions (I)-(III)]. It is therefore natural to assume that molecular nitrogen is a mild oxidation product, while nitrogen oxides are products of the extensive oxidation (NO is a more oxidised species than N_2O).

At the same time, there is a difference between the ammonia and organic substance oxidation reactions, involving their thermodynamics. In the oxidation of organic compounds, the products of extensive oxidation are thermodynamically more resistant to further oxidation than the mild oxidation products. In the oxidation of ammonia, the opposite situation obtains, as can be seen from a comparison of the standard heats of reactions (I) to (III) (when the entropy change is taken into account, the situation does not change). This feature of the thermodynamics of the reactions is manifested by the fact that completion of the oxidation of a mild oxidation product by molecular oxygen involves a consecutive reaction mechanism in the oxidation of organic substances, while in the oxidation of ammonia the reduction of the product of extensive oxidation by the initial oxidisable substance proceeds via this mechanism:

$$2NH_3 + 3N_2C = 4N_2 + 3H_2O, \tag{IV}$$

$$2NH_3 + 8NO = 5N_2O + 3H_2O, \tag{V}$$

$$2NH_3 + 3NO = 2\frac{1}{2}N_2 + 3H_2O. \tag{VI}$$

This feature has a significant influence on the process kinetics.

The data discussed in this review have been divided on the basis of the principal types of ammonia oxidation catalysts (metals, their alloys, simple oxides, complex and promoted oxide catalysts, zeolites). The usefulness of such subdivisions follows from the fact that the most clear-cut relations between the catalytic and physicochemical properties of the relevant substances are to be expected within a group of similar catalysts for this process. Each section is arranged as follows: data on the catalytic properties (activity and selectivity series) are considered first, next the chemical kinetics and reaction mechanism are discussed, and finally the problem of the relation between the catalytic and physicochemical properties of substances of the given type is analysed on this basis.

II. OXIDATION OF AMMONIA IN THE PRESENCE OF VARIOUS CATALYSTS

1. Oxidation of Ammonia in the Presence of Metals

The catalytic properties of various metals in the oxidation of ammonia under kinetic conditions have been investigated[4,5]; the experiments were carried out at low temperatures (up to 370°C), where the reaction products are N_2 and N_2O. Table 1 shows that at 300°C the specific catalytic activity of metals for the overall process decreases in the sequence†

$$Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti.$$

In general, there is a similarity between this series and the series observed in the oxidation of hydrogen[6] (Pt > Pd > Ni > Fe > Cu > Ag > Au > Ti), gas containing SO_2 [7] (Pt > Pd > Au > W), and lower olefins[8] (Pt > Pd > Au > W). At high temperatures (500–700°C), the activity of platinum in the oxidation of ammonia exceeds those of rhodium, palladium, and iridium[9].

An effect of the reaction medium on copper, titanium, and tungsten, leading to partial oxidation of these metals, has been noted[5]. At high temperatures, this effect is intensified and platinum and other metals become susceptible to it[1]. The oxidation of ammonia in the presence of platinum begins at temperatures of the order of 150 to 200°C. Under these conditions, the only nitrogen-containing reaction product is molecular nitrogen. With increase of temperature, nitrous oxide appears in the products, its yield passing through a maximum. At temperatures of the order of 300°C, nitric oxide begins to form; its yield increases with temperature and can reach 90% at 700 to 1000°C. Under conditions favourable for the synthesis of NO, the reaction takes place under diffusion-limited conditions[1,2].

Table 1. The oxidation of ammonia in the presence of metals*.[4,5]

Catalyst	r, mol. cm^1 s^{-1}, (at 300°C)	E, kcal mole^{-1}	Temperature of onset of formation, °C	
			N_2	N_2O
Pt	$1.70 \cdot 10^{17}$	27	195	215
Pd	$2.69 \cdot 10^{16}$	5	100	150
Cu	$3.31 \cdot 10^{15}$	12	175	260
Ag	$2.52 \cdot 10^{15}$	15	200	210
Ni	$1.23 \cdot 10^{15}$	12	210	270
Au	$8.32 \cdot 10^{14}$	4	180	300
Fe	$6.76 \cdot 10^{14}$	9	230	270
W	$5.90 \cdot 10^{14}$	13	225	300
Ti	$2.24 \cdot 10^{14}$	5	180	**

*Composition of reaction mixture: $p_{NH_3} = 0.1$ atm; $p_{O_2} = 0.9$ atm.

**Up to 370°C, nitrous oxide is not formed.

A similar behaviour has been observed also in the presence of other metallic catalysts. Table 1 shows that, for each metal, nitrogen begins to form at a lower temperature than nitrous oxide. NO is formed at still higher temperatures[1].

At low temperatures (Table 1), the process takes place under kinetic conditons and the ammonia oxidation products in the presence of various metals are N_2 and N_2O. Under these conditions, the selectivity with respect to nitrous oxide increases with temperature[4,5]. In the presence of transition metals, the selectivity with respect to this product increases in the sequence

$$Pt, Pd > Ni > Fe > W > Ti,$$

i.e. the selectivity in relation to the extensive oxidation of ammonia varies in parallel with the catalytic activity in the overall process[5]. Experimental studies on the mechanism of the oxidation of ammonia in the presence of metals have been carried out mainly in recent years. In previous studies, a multiplicity of hypothetical mechanisms were put forward, postulating the intermediate formation of species such as NH_2OH, HNO, NH, and others (see the review of Dixon and Longfield[2]). However, these mechanisms were not supported by experimental evidence, which is the reason for their abundance.

In order to elucidate the composition of the intermediate surface complexes formed in the catalytic oxidation of ammonia, the composition of the species generated when the NH_3–O_2 mixture interacts with metals and the species desorbed from their surface following the application of a strong electric field was investigated[10] by autoionisation mass-spectrometry. The experiments were performed using emitters in the form of a platinum needle and a

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†Below 250°C, palladium is more active than platinum.[5]

tungsten filament; some of the experiments were performed using ammonia labelled with ^{15}N. Apart from the ions corresponding to the starting materials and the final reaction products, those of the intermediate HNO and NH (nitroxyl and imide) formed on the surface were also detected.

The kinetics of the oxidation of ammonia on massive platinum have been studied[4] by the flow method (for conversions not exceeding 15%) and by the flow-circulation method at atmospheric pressure. The experiments were performed under conditions where the products were N_2 and N_2O. The partial pressure of ammonia in the reaction mixture (p_{NH_3}) was varied in the range 0.05–0.20 atm and the partial pressure of oxygen (p_{O_2}) was varied in the range 0.20–0.95 atm; the ratio p_{O_2}/p_{NH_3} was varied from 1 to 18.9. The results refer to the steady state of the catalyst. The study of the temperature variation of the reaction rate revealed a sharp and abrupt increase of the rate on reaching 240°C. This was accompanied by a rapid and marked increase in the catalyst temperature. Such effects were observed for different compositions of the reaction mixtures, different flow rates, and in experiments using both the flow and flow-circulation methods. The results discussed below[4] refer to the temperature range where the above complications are absent.

At temperatures up to 230°C, the rates of reactions (I) and (II) and selectivity are independent of contact time (for virtually constant p_{NH_3} and p_{O_2}). This implies that nitrogen and nitrous oxide are formed simultaneously under these conditions. At the same time it also follows that the reaction products whose concentration varies severalfold do not influence the rate of oxidation of ammonia.

The variation of the rate of the overall process and of the rates of formation of the individual products (r_{N_2} and r_{N_2O}) with p_{NH_3} and p_{O_2} is described by hyperbolic curves. For low values of p_i, the rates are proportional to the p_i (first-order reaction), while, for high values of p_i, the rates are virtually independent of the latter (zero-order reaction). The attempts to describe the observed variation by kinetic equations of the Langmuir–Hinshelwood type were unsuccessful. Taking into account the results of a mass-spectrometric study of the composition of the intermediates formed on the surface of platinum and tungsten during the catalytic oxidation of ammonia[10] and data on the sorption of oxygen on platinum, the authors[4,11] proposed the following reaction mechanism‡:

$$\begin{array}{lcc}
 & N^{(\mathrm{I})} & N^{(\mathrm{II})} \\
1)\ O_2 + (\ ) \rightarrow (O_2) \xrightarrow[\text{fast}]{(\ )} 2\,(O) & 1\frac{1}{2} & 2 \\
2)\ NH_3 + (O) \rightarrow (NH) + H_2O & 2 & 2 \\
3)\ (NH) + (O) \rightleftarrows (HNO) & 1 & 2 \\
4)\ (NH) + (HNO) \rightarrow N_2 + H_2O + 3\,(\ ) & 1 & 0 \\
5)\ (HNO) + (HNO) \rightarrow N_2O + H_2O + 4\,(\ ) & 0 & 1 \\
\hline
N^{(\mathrm{I})}: 2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O & & \\
N^{(\mathrm{II})}: 2NH_3 + 2O_2 = N_2O + 3H_2O & &
\end{array} \qquad \text{(VII)}$$

The reaction proceeds via two kinetically independent routes $N^{(\mathrm{I})}$ and $N^{(\mathrm{II})}$, the corresponding sets of the stoichiometric numbers of the stages being shown on the right-hand side of scheme (VII) and the overall chemical equations (I) and (II). The first stage of the process involves the chemisorption of oxygen with intermediate formation of the anion $(O^2)^-$; on the basis of the available data[12], it is suggested that the adsorption of O_2 on platinum at 200–250°C leads ultimately to the formation of atomic oxygen ions (O) having a negative charge. This stage is irreversible. In the second stage, ammonia molecules react with the surface coated by oxygen and form adsorbed species (NH), which are converted in the third (quasi-reversible) stage into the surface nitroxyl (HNO). Analysis of the kinetic data[13] suggests that the (NH) species occupies one elementary surface site and the (HNO) species two such sites. Since the catalyst gives up electrons to the adsorbed oxygen in the first stage, it is natural to assume that, in the interaction of ammonia with platinum coated by oxygen, electrons are transferred from ammonia to the catalyst. The final reaction products in the last two stages are N_2 from (NH) and (HNO), on the one hand, and N_2O from two nitroxyls, on the other.

The following kinetic equations for the rate of the overall process r, the steady-stage degree of surface coverage by atomic oxygen θ, and the selectivities with respect to N_2 and N_2O (S_{N_2} and S_{N_2O}) correspond to the above process mechanism[13]:

$$r = \frac{1}{2} k_2 p_{NH_3} \theta = \frac{1}{2} k_1 k_2 p_{O_2} p_{NH_3} / (k_1 p_{O_2} + \bar{\nu} k_2 p_{NH_3}), \tag{1}$$

$$\theta = \frac{k_1}{k_2} \frac{p_{O_2}}{p_{NH_3}} \Big/ \left(\frac{k_1}{k_2} \frac{p_{O_2}}{p_{NH_3}} + \bar{\nu} \right), \tag{2}$$

$$S_{N_2} = \frac{\mu}{\mu + \theta}, \tag{3}$$

$$S_{N_2O} = \frac{\theta}{\mu + \theta}, \tag{4}$$

where

$$\mu = k_4 / k_5 K_3. \tag{5}$$

In these equations, k_i are the rate constants for the various stages, K_3 is the equilibrium constant for the first stage, and $\bar{\nu}$ is a stoichiometric coefficient showing how many O_2 molecules are consumed on average in the oxidation of one NH_3 molecule; the experimental value[4] is $\bar{\nu} = 0.78 \pm 0.02$. Eqns. (1)–(4) have been derived on the assumption that the reaction proceeds in an ideal monolayer and that the degree of surface coverage by atomic oxygen is much greater than the coverage by other species.

Fig. 1 shows that Eqn. (1), according to which the relation between p_{O_2}/r and p_{O_2}/p_{NH_3} should be linear, describes satisfactorily the variation of r with the composition of the reaction mixture. The slope of the straight line is $2/k_2$ and its intercept on the ordinate axis is $2\bar{\nu}/k_1$. Hence k_1 and k_2 were calculated. The temperature variation of these constants obeys the Arrhenius equation and the heats of activation for the first two stages are $E_1 = E_2 = 32$ kcal mole^{-1}.

Eqns. (3) and (4) show that, at a constant temperature, the selectivity of the given catalyst should be determined by the degree of surface coverage by oxygen θ, which depends in its turn on the mixture composition, i.e. on the ratio p_{O_2}/p_{NH_3}. It follows from Eqn. (2) that θ increases with increase of p_{O_2}/p_{NH_3} ($\theta \rightarrow 0$ when $p_{O_2}/p_{NH_3} \rightarrow 0$ and $\theta \rightarrow 1$ when $p_{O_2}/p_{NH_3} \rightarrow \infty$). It is expected that, with increase of p_{O_2}/p_{NH_3}, i.e. with the increase of θ, the selectivity with respect to the mild oxidation product (nitrogen) should fall continuously $[dS_{N_2}/d\theta = -\mu/(\mu + \theta)^2 < 0]$ and that the selectivity with respect to the extensive oxidation product (nitrous oxide) should increase ($dS_{N_2O}/d\theta = -dS_{N_2}/d\theta > 0$). Eqns. (3) and (4) predict that when $\theta \rightarrow 0$, i.e. when $p_{O_2}/p_{NH_3} \rightarrow 0$,

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‡Here and henceforth the symbols for substances enclosed in brackets denote surface species, while brackets enclosing a blank space denote free surface sites.

S_{N_2} tends to unity and S_{N_2O} tends to zero. When $\theta \to 1$ (for high values of p_{O_2}/p_{NH_3}), S_{N_2} and S_{N_2O} tend to constant values, which are respectively $\mu/(\mu+1)$ and $1/(\mu+1)$. The quantity μ can be calculated from the values of S_i and p_{O_2}/p_{NH_3} for a single experiment by Eqn. (3) or (4) [taking into account Eqn. (2)] and then the variation of the selectivity with θ (or with p_{O_2}/p_{NH_3}) may be calculated for a wide range of compositions of the reaction mixture. The results of such calculations are presented in Fig. 2 (in the form of continuous curves). The satisfactory agreement with experiment (circles in Fig. 2) demonstrates the validity of Eqns. (3) and (4).

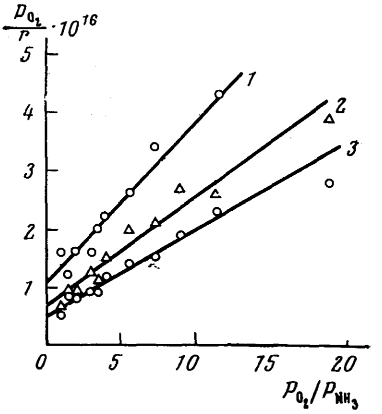

Figure 1. Variation of p_{O_2}/r with p_{O_2}/p_{NH_3} in the presence of a platinum catalyst[4] at different temperatures (°C): 1) 220; 2) 225; 3) 230.

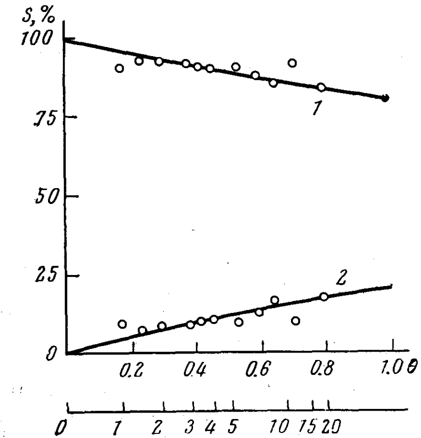

Figure 2. Variation of the selectivity with respect to N_2 (line 1) and N_2O (line 2) with p_{O_2}/p_{NH_3} and θ at 230°C on a platinum catalyst[4] ($\mu = 3.8$; $k_1/k_2 = 0.2$).

Thus the experimental kinetic data agree with scheme (VII). Hence it follows that this scheme reflects the essential features of the reaction mechanism on the platinum catalyst.

With increase of temperature, the parallel-reaction mechanism of the oxidation of ammonia is converted into a parallel-consecutive-reaction mechanism; at 235°C, an increase in contact time entails a decrease of selectivity with respect to N_2O. This has been explained[4] by the fact that, for fairly high values of p_{N_2O}, in addition to reactions (I) and (II), reaction (IV) also occurs, leading to the conversion of a definite proportion of the nitrous oxide formed into nitrogen. The probable process mechanism under these conditions can be described as follows[4]:

$$\begin{array}{lccc} & N^{(I)} & N^{(II)} & N^{(IV)} \\ 1)\ O_2 + (\ ) \xrightarrow[\text{fast}]{} (O_2) \xrightarrow[\text{fast}]{(\ )} 2\,(O) & 1\frac{1}{2} & 2 & 0 \\ 2)\ NH_3 + (O) \to (NH) + H_2O & 2 & 2 & 2 \\ 3)\ (NH) + (O) \rightleftarrows (HNO) & 1 & 2 & 1 \\ 4)\ (NH) + (HNO) \to N_2 + H_2O + 3\,(\ ) & 1 & 0 & 1 \\ 5)\ (HNO) + (HNO) \to N_2O + H_2O + 4\,(\ ) & 0 & 1 & 0 \\ 6)\ N_2O + (\ ) \to (O) + N_2 & 0 & 0 & 3 \end{array} \qquad \text{(VIII)}$$

$$N^{(I)}: 2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O\ ;$$

$$N^{(II)}: 2NH_3 + 2O_2 = N_2O + 3H_2O\ ;$$

$$N^{(IV)}: 2NH_3 + 3N_2O = 4N_2 + 3H_2O\,.$$

The reaction proceeds via three fundamental routes, $N^{(I)}$, $N^{(II)}$, and $N^{(IV)}$, to which the overall Eqns. (I), (II), and (IV) correspond. Scheme (VIII) is obtained from scheme (VII) when the latter is supplemented by a sixth stage, in which nitrous oxide is irreversibly converted on the surface into adsorbed oxygen and N_2. The (O) atoms formed in this stage subsequently react with NH_3, together with the (O) atoms generated in the first stage as a result of the adsorption of molecular oxygen. It has been shown[4] that, under the experimental conditions used in the oxidation of ammonia, the rate of desorption of oxygen formed in stages (1) and (6) can be regarded as extremely small compared with the rates of the forward reactions in these stages.

The application of the theory of complex steady-state reactions[14] to scheme (VIII) taking into account the postulates noted above leads to the following selectivity equations[4]:

$$S_{N_2} = \frac{r_{N_2}}{r} = \frac{r^{(I)} + 4r^{(IV)}}{r} = \frac{\mu}{\mu+\theta} + \frac{2\bar{\nu}k_6}{k_1}\,\frac{p_{N_2O}}{p_{O_2}}\,, \tag{6}$$

$$S_{N_2O} = \frac{r_{N_2O}}{r} = \frac{r^{(II)} - 3r^{(III)}}{r} = \frac{\theta}{\mu+\theta} - \frac{2\nu k_6}{k_1}\,\frac{p_{N_2O}}{p_{O_2}}\,, \tag{7}$$

where $r^{(I)}$, $r^{(II)}$, and $r^{(IV)}$ are the rates of the reactions via routes $N^{(I)}$, $N^{(II)}$, and $N^{(IV)}$, while the remaining quantities have the previous significance. The expressions for r and θ are again determined by Eqns. (1) and (2).

By oxidising ammonia using the flow-circulation method with virtually constant p_{NH_3}, p_{O_2}, and θ but significantly variable values of p_{N_2O}, the authors[4] established that the selectivity with respect to N_2O decreases linearly with increase of p_{N_2O}, which confirms the validity of Eqns. (6) and (7). The latter equations can be put in the form

$$S_{N_2} = (S_{N_2})_0 + \Delta, \qquad S_{N_2O} = (S_{N_2O})_0 - \Delta, \tag{8}$$

where $(S_{N_2})_0$ and $(S_{N_2O})_0$ are the selectivities with respect to N_2 and N_2O when the reaction proceeds exclusively via the parallel-process mechanism [Eqns. (3) and (4)] and

$$\Delta = \frac{2\bar{\nu}k_6 p_{N_2O}}{k_1 p_{O_2}} = \frac{2\bar{r}_6}{r_1} \tag{9}$$

reflects the change in selectivity caused by the appearance of the consecutive-reaction mechanism (IV); this quantity is determined by the ratio of the rates of the sixth and first stages. Eqn. (9) shows that the higher the rate of decomposition of N_2O compared with the rate of absorption of O_2, the greater the contribution to the observed selectivity by the consecutive-reaction scheme; in this case, the dominant source of adsorbed oxygen is N_2O and not O_2. A decrease of contact time leads to a decrease of p_{N_2O}, so that, when $\tau \to 0$, i.e. when $p_{N_2O} \to 0$, Δ tends to zero—the parallel-reaction mechanism obtains exclusively [Eqns. (6) and (7) are identical with Eqns. (3) and (4)].

As mentioned above, when the temperature is raised appreciably, NO appears in the reaction products in addition to N_2 and N_2O, i.e. all three processes (I)–(III) take place at once. At temperatures in the range 700 to 1000°C in the presence of platinum catalysts, mainly NO is formed. At the same time, the process is inhibited by diffusional factors, since the overall rate of reaction increases sharply. For the stoichiometric [in relation to reaction (III)] $O_2 : NH_3$ ratio, the observed rate of oxidation of ammonia is determined by the rate of diffusion of oxygen to the outer surface of the massive catalyst (gauze); in the presence of an excess of oxygen relative to stoichiometry of more than 30%, the diffusion of ammonia is rate-limiting[1].

As a result of macrokinetic inhibition of this kind, the kinetics and mechanism of the reaction at high temperatures, i.e. under conditions where reaction (II) also occurs, have been scarcely investigated experimentally. One can only mention one study[15] where the oxidation of ammonia was investigated on platinum at low pressures (where the diffusion of gases if facilitated) and it was shown that the rate of the overall process is described by the first-order equation

$$r = kp^1_{NH_3}p^0_{O_2}. \tag{10}$$

Despite the lack of the necessary experimental data (which will evidently become available in the future), it is useful to discuss the problem of the probable behaviour which may be expected when reactions (I)–(III) occur simultaneously under kinetic conditions and provided that a parallel-process and purely heterogeneous mechanism operates. In this case the following mechanism can be postulated[13]:

$$\begin{array}{llccc}
 & & N^{(I)} & N^{(II)} & N^{(III)} \\
1)\ O_2 + (\ ) & \to (O_2) \xrightarrow[\text{fast}]{(\ )} 2(O) & 1\frac{1}{2} & 2 & 2\frac{1}{2} \\
2)\ NH_3 + (O) & \to (NH) + H_2O & 2 & 2 & 2 \\
3)\ (NH) + (O) & \rightleftarrows (HNO) & 1 & 2 & 2 \\
4)\ (NH) + (HNO) & \to N_2 + H_2O + 3(\ ) & 1 & 0 & 0 \\
5)\ (HNO) + (HNO) & \to N_2O + H_2O + 4(\ ) & 0 & 1 & 0 \\
6)\ 2(HNO) + (O) & \to 2NO + H_2O + 5(\ ) & 0 & 0 & 1 \\
\hline
\end{array} \qquad (IX)$$

$$N^{(I)} : 2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O;$$

$$N^{(II)} : 2NH_3 + 2O_2 = N_2O + 3H_2O;$$

$$N^{(III)} : 2NH_3 + 2\frac{1}{2}O_2 = 2NO + 3H_2O.$$

Scheme (IX) is obtained from scheme (VII) when the latter is supplemented by the postulated stage (6)§, which results in the appearance of a third reaction pathway $N^{(III)}$ and the overall Eqn. (III) applies.

Eqn. (I) for the overall rate of the process remains unchanged under these conditions. The equations for the selectivity then become

$$S_{N_2} = \frac{\mu}{\mu + \theta + \mu'\theta^2}, \tag{11}$$

$$S_{N_2O} = 1 - \frac{\mu}{\mu + \theta + \mu'\theta^2} - \frac{\theta}{1/\mu' + \theta + \mu/\mu'\theta}, \tag{12}$$

$$S_{NO} = \frac{\theta}{1/\mu' + \theta + \mu/\mu'\theta}, \tag{13}$$

where μ is again defined by Eqn. (5) and $\mu' = k_6'/k_5$ [k_6' is the rate constant for the sixth stage in scheme (IX)].

The heat of the sixth stage is significantly smaller than that of the fifth stage. Indeed the difference between the heats of these stages is $q_6 - q_5 = 2q_{NO} - q_{(O)} - q_{N_2O}$, where q_i are the heats of formation of the reactants; the difference $2q_{NO} - q_{N_2O} = -23.7$ kcal[16] is negative and, since the heat of adsorption of oxygen $q_{(O)} > 0$, the difference $q_6 - q_5$ is significantly smaller than zero. On the basis of the Brønsted–Temkin relation, the heat of activation for this stage is the higher the lower is its heat of reaction. For this reason, the heat of activation for the sixth stage is higher than for the fifth stage, so that μ' increases with temperature. If the temperature is low, μ' is close to zero; Eqn. (13) shows that, under these conditions, $S_{NO} \simeq 0$ and Eqns. (11) and (12) become identical with Eqns. (3) and (4). At high temperatures, μ' is high and S_{NO} is considerable. This is consistent with the fact that the oxidation of NH_3 to NO is as a rule carried out at high temperatures.

Eqns. (11)–(13) have the following consequences. For mixtures rich in ammonia (when $p_{O_2}/p_{NH_3} \to 0$ and $\theta \to 0$), $S_{N_2} \to 1$ and S_{N_2O} and S_{NO} tend to zero. With increase in the excess of oxygen in the reaction mixture (with increase of θ), S_{N_2} falls, tending to the constant value $\mu/(\mu + 1 + \mu')$ (when $\theta = 1$), while S_{NO} increases, tending to the corresponding limit $\mu'/(\mu + 1 + \mu')$. The variation of S_{N_2O} with θ is more complex: for fairly large values of μ', it passes through a maximum. To illustrate all these findings, Fig. 3 presents the results of a model calculation of the variation of the selectivity with θ and p_{O_2}/p_{NH_3} when $\mu' = 100$ (continuous curves) and $\mu' = 10$ (dashed curves); it was assumed in both cases that $k_1/k_2 = 1$, $\bar{\nu} = 1$, and $\mu = 1$. Evidently, the higher the value of μ', the higher the selectivity with respect to NO, and the lower the selectivity with respect to N_2 and N_2O.

In order to test the theoretical calculations, it is necessary to investigate the kinetics of the oxidation of ammonia at elevated temperatures under conditions ruling out the influence of transport processes and of consecutive reactions of the products. The theoretical and experimental data can already be compared to some extent. Thus Eqn. (10) for the rate of the overall process, corresponding to high temperatures of the catalytic reaction on platinum[15], is the same as Eqn. (1): with $k_1p_{O_2} \gg \bar{\nu}k_2p_{NH_3}$, Eqn. (1) becomes identical with Eqn. (10). The dependence of the selectivity with respect to NO on p_{O_2}/p_{NH_3} observed at 900°C on platinum[1] is very close to that illustrated in Fig. 3. Since the process is distorted by the influence of external diffusion under these conditions, the above comparison is not rigorous, but can nevertheless serve as an argument in support of Eqn. (13).

For a complete description of the reaction kinetics under conditions corresponding to the formation of N_2, N_2O, and NO, it is necessary to take into account the

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§Experimental data justifying the above formulation of stage (6) are as yet unavailable; it is possible to postulate other versions, for example (HNO) + (O) → NO + (OH) + 2 ( ) with subsequent conversion of (OH) into H_2O, etc.

interaction of NH_3 with NO, i.e. reactions (V) and (VI), in addition to reactions (I)–(IV). The kinetics of the platinum-catalysed reaction (VI) have been investigated[17] and it has been shown that the reaction is strongly inhibited by oxygen. The mechanism of reactions (V) and (VI) on platinum has been studied by the isotopic tracer method[18]. The authors[18] concluded that, in the course of the above reactions at 200°C, NH_3 molecules dissociate on the surface of platinum with formation of the (NH_2) species, which then react with NO, yielding N_2 and H_2O. At high temperatures, further dissociation of (NH_2) with formation of (NH) is postulated.

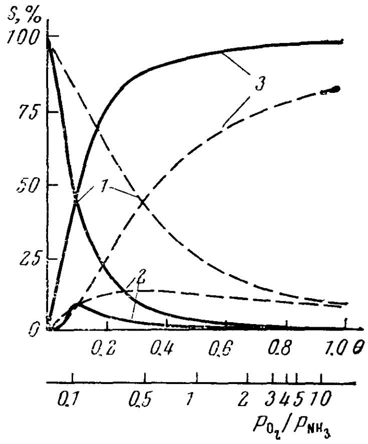

Figure 3. Variation of S_{N_2} (curve *1*), S_{N_2O} (curve *2*), and S_{NO} (curve *3*) with mixture composition[13,46].

The second stage in schemes (VII)–(IX), reflecting the interaction of NH_3 with adsorbed oxygen, is probably in reality more complex than would follow from the equation quoted for this stage. Possibly the formation of the (NH) species from NH_3 and (O) is preceded by the activation of the ammonia molecules on the metal surface free from oxygen[4,5]. This hypothesis is confirmed by the finding that mechanical admixtures of platinum to cobalt, manganese, and vanadium oxides accelerate their reduction by ammonia[19]. The activation of NH_3 molecules on the surface of platinum and other transition metals may involve the dissociation (or marked weakening) of the N–H bond. As pointed out by the present author and Golodets[4,5], this is supported by the fact that transition metals actively catalyse the NH_3–D_2 exchange, although this happens at temperatures lower than those corresponding to the oxidation of NH_3: the exchange between NH_3 and D_2 involves an intermediate stage with partial dissociation of ammonia molecules[20]. As mentioned above, it is natural to suppose that ammonia behaves as an electron donor in its reaction with (O). The conclusion that electrons are transferred from the adsorbed ammonia molecules to the metal follows from a study[21] where the adsorption of NH_3 on gold was investigated by electrophysical methods.

All the schemes described presuppose a purely heterogeneous mechanism of the oxidation of ammonia. Many investigators have considered the possibility of a heterogeneous-homogeneous mechanism of this reaction on platinum, particularly at high temperatures[1,2]. It has been concluded[22,23] that this process is transferred to the bulk phase. It was mentioned above that an abrupt acceleration to the process on platinum has been observed[4] on reaching 240°C. Similar "critical" phenomena have been observed in another investigation[24]. One of their likely causes, according to the present author and Golodets[4], is the transfer of the process to the bulk phase, where the reaction proceeds via a radical-chain mechanism. On the other hand, other investigators (see, for example, Epshtein[25] and Nutt and Kapur[26]) reject a heterogeneous-homogeneous mechanism of the oxidation of ammonia. Thus Nutt and Kapur[26], using mass-spectrometric analysis, failed to detect the presence in the gas phase of unstable intermediate species which might serve as the active centres for the bulk-phase chains in the catalytic oxidation of ammonia; they carried out the catalytic process on platinum at low pressures over a wide range of temperatures (up to 1300°C).

Evidently the discrepancies between the conclusions reached in different investigations can be largely attributed to different experimental conditions. The problem of the role of bulk-phase chains in the mechanism of the catalytic oxidation of ammonia requires further study under conditions as close as possible to the usual conditions in the catalytic process.

We shall now consider the problem of the relation between the catalytic properties of metals in the oxidation of ammonia and their physicochemical (thermodynamic) properties. The discussion may be based[27,28] on mechanism (VII) and the corresponding kinetic equations (1)–(4).

It is natural to suppose that the mechanisms of reactions occurring on different transition metals are similar. This is indicated, in particular, by the finding that the compositions of the intermediate nitrogen compounds desorbed from the platinum and tungsten surfaces after the catalytic process are similar[10]. The differences between the catalytic activities and selectivities of different metals for a constant composition of the reaction mixture and temperature are determined by the differences between the constants in Eqns. (1)–(4).

The relation between the rate constants for different stages and the thermodynamic characteristics of the catalysts is given by the Brønsted–Temkin equation

$$k_i = g_i K_i^{\alpha_i} = g_i \exp\left(\frac{\alpha_i \Delta S_i^0}{R}\right)\cdot\exp\left(\frac{\alpha_i q_i}{RT}\right), \qquad (14)$$

where K_i is the equilibrium constant for the ith stage, q_i the heat of this stage, ΔS_i^0 the standard entropy of the stage, and g_i and α_i are constants for a number of similar catalysts for the given process (ΔS_i^0 in the given series may be regarded as approximately constant[29]).

A common feature of the different stages of mechanism (VII) is that they involve the formation or dissociation of the oxygen–catalyst bond. Consequently, the catalytic activity and selectivity should depend significantly on the energy of this bond, which may be measured by the heat q_S of the binding of oxygen to the surface[30]: $\frac{1}{2}O_2 + (\ ) = (O)$. At the same time, bonds between the catalyst and other atoms (for example, nitrogen) may be formed and dissociated during the reactions. The approximation employed is that the energies of these bonds change much less on passing from one catalyst to another than the q_S.[32] The fact that the energy of the metal–oxygen bond depends much more markedly on the nature of the metal than those of the metal–nitrogen and metal–hydrogen bonds is an argument in support of this hypothesis[31]. Furthermore, since the typical value of the coefficient α in Eqn. (14) is 0.5, [29] we shall assume that the α_i for different stages are the same and equal to α, which somewhat simplifies the analysis.

The variation of the catalytic activity with q_S is described by the function $\rho = \partial \ln r/\partial q_S$ for T, p_i = const., where r is defined by Eqn. 1. On differentiating Eqn. (1)¶ and taking into account Eqn. (14) as well as the fact that $q_1 = 2q_S$ and $q_2 = q'_2 - q_S$ (where q'_2 is a combination of the terms of the approximation employed), we obtain

$$\rho = \frac{\alpha}{RT}(2-3\theta). \tag{15}$$

Here

$$\theta = \left[1 + \frac{\bar{\nu}}{A}\exp\left(-\frac{3\alpha}{RT}q_s\right)\right]^{-1}, \tag{16}$$

where A is a constant. The last equation shows that θ increases with increase of q_S, tending to unity. If the range of variation of q_S is fairly large, then the variation of $\ln r$ with q_S passes through a maximum, since $\rho > 0$ when $\theta \to 0$ and $\rho < 0$ when $\theta \to 1$. The maximum corresponds to $\rho = 0$, whence the optimum value of θ is 2/3 according to Eqn. (15). This implies that, in the group of similar catalytic systems, the catalyst for which q_S corresponds to $\theta = 2/3$ exhibits the highest specific activity at the given temperature and for the given mixture composition.

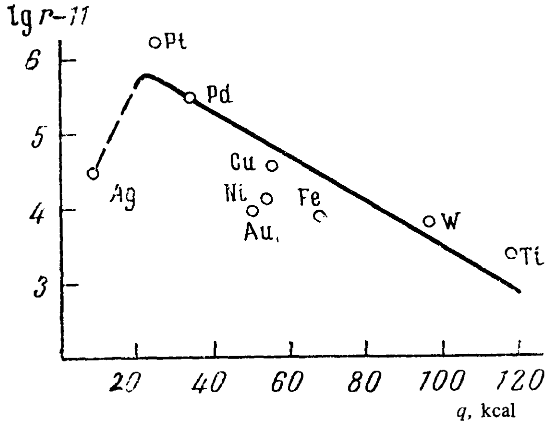

Figure 4. Variation of the specific catalytic activity of metals in the oxidation of NH_3 at 300°C with the energy q_S of the bond between the catalyst and oxygen[30]; mixture composition: $p_{NH_3} = 0.1$ atm; $p_{O_2} = 0.9$ atm.[5]

In the region where θ is close to unity (this is attained by carrying out the catalyst process in the presence of a large excess of O_2), the variation of $\ln r$ with q_S should be represented by a straight line with a negative slope:

$$\rho = -\alpha/RT, \tag{17}$$

i.e. the specific activity should fall steadily as q_S increases. Fig. 4 shows that this is indeed observed. It follows from Eqn. (1) that in this region $r \simeq \frac{1}{2}k_2 p_{NH_3}$, i.e. the decrease of the activity with increasing q_S is caused by the fact that the rate is determined by stage (2), where the bond between oxygen and the catalyst dissociates. The observed relation between $\log r$ and q_S is analogous to corresponding relations found earlier [30] for the oxidation of hydrogen, carbon monoxide, and organic substances.

The type of variation of the selectivity with q_S is determined, as can be seen from Eqns. (3) and (4), by the dependence of θ and μ on q_S. Using Eqn. (14) to determine k_4 and k_5 and taking into account Eqn. (5), we obtain

$$\mu = B\exp\left[\frac{\alpha}{RT}(q^4 - q^5)\right]\cdot\exp\left(-\frac{q_3}{RT}\right), \tag{18}$$

where B combines a number of constants. Assuming, as before, that on passing from one catalyst to another, mainly the values of q_S change, we have

$$q_4 = q'_4 - n_{N_2}q_s,\quad q_5 = q'_5 - n_{N_2O}q_s,\quad q_4 - q_5 = q' + (n_{N_2O} - n_{N_2})\,q_s.$$

In these equations, q'_4, q'_5, and q' combine terms independent of q_S and n_{N_2} and n_{N_2O} are coefficients determined by the number of oxygen–catalyst bonds dissociated in stages (4) and (5). In terms of the approximation employed, q_3 may be regarded as independent of q_S, since in the third stage the oxygen–catalyst bond is both dissociated and formed. We then obtain in place of Eqn. (18)

$$\mu = \mu_0 \exp(\alpha\,\Delta n q_s/RT), \tag{19}$$

where μ_0 is independent of q_S and Δn is

$$\Delta n = n_{N_2O} - n_{N_2}. \tag{20}$$

Fewer oxygen–catalyst bonds are dissociated in stage (4) than in stage (5), so that $\Delta n > 0$; consequently the coefficient μ increases with increase of q_S and so does θ [Eqn. (16)]. The selectivity with respect to N_2 should therefore increase with increase of q_S, tending to unity, while the selectivity with respect to N_2O should fall, tending to zero. Fig. 5 shows that such a relation is indeed observed.

Thus the principal cause of the increase of selectivity with respect to the mild oxidation product as q_S increases is that the formation of this product (the fourth stage) entails the dissociation of fewer oxygen–catalyst bonds than in the formation of the extensive oxidation product (the fifth stage).

This approach can be extended to a more general stage where NH_3 is oxidised to N_2, N_2O, and NO [scheme (IX), Eqns. (11)–(13)]. In this case, the behaviour expected on the basis of the theory is as follows [27,28]: with increase of q_S, the selectivity with respect to the mild oxidation product (N_2) should rise continuously and that with respect to the extensive oxidation product (NO) should fall. This is confirmed qualitatively by the observation that, at fairly high temperatures, platinum exhibits a higher selectivity with respect to NO than palladium, rhodium [9], and other transition metals [1] characterised by higher values of q_S than platinum.

On the basis of the Polanyi relation for the heats of activation and the hypothesis that the higher the degree of oxidation of the product the greater number of oxygen–catalyst bonds dissociated in the stage leading to its formation, one can show [33] that the heat of activation for the reactions under consideration (in the presence of the given catalyst) should increase in the sequence $E_{N_2} < E_{N_2O} < E_{NO}$. The temperatures of the onset of the formation of the corresponding products should therefore increase in the same sequence. This conclusion is confirmed by

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¶ Since the coefficient $\bar{\nu}$ usually varies within narrow limits, in our discussion it is permissible to disregard this variation of $\bar{\nu}$ with q_S.

the data in Table 1 and by the finding[1] that NO begins to be formed at higher temperatures than N_2O in the presence of each metal.

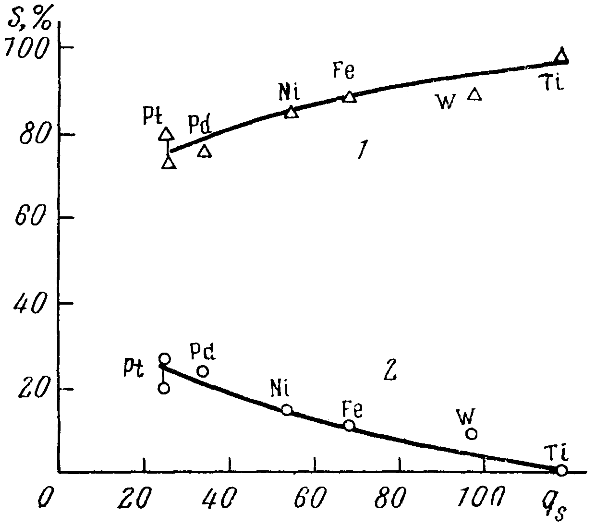

Figure 5. Variation of the selectivity of transition metals at 300°C with q_S (Il'chenko et al.[5]): 1) selectivity with respect to N_2; 2) selectivity with respect to N_2O.

The observed decrease with q_S of both characteristics—the activity r with respect to the overall process and the selectivity S_{N_2O} with respect to the extensive oxidation of NH_3 (see Figs. 4 and 5)—explains the empirical relation noted previously, namely the parallel variation of r and S_{N_2O}.

2. Oxidation of Ammonia in the Presence of Metallic Alloys

In the oxidation of ammonia to NO under industrial conditions, platinum is strongly acted upon by the reaction mixture, under the influence of which the surface of the platinum gauze is loosened, the gauze becomes brittle, and gradually breaks up. The attention of the investigators has therefore been directed to the search for additives to platinum which would improve its strength and stability without reducing its catalytic activity and selectivity. Such requirements are satisfied by platinum–rhodium alloys. In practice, one uses gauze made of 90% Pt–10% Rh alloy (owing to the high cost of rhodium, alloys containing 5–7% Rh are sometimes used). When the reaction is carried out at atmospheric pressure, platinum alloys with 4% Pd and 3.5% Rh, which are somewhat less stable but no less active than the platinum–rhodium catalysts, are employed. Other platinum (and palladium) alloys with transition metals, particularly the platinum alloy with 1% 1% Ir, [1] also exhibit a high activity in the oxidation of ammonia to NO.

Systematic studies yielding information about the specific catalytic activities of alloys and their selectivities under kinetic conditions (particularly at low temperatures) have not so far been made. The kinetics and mechanism of the oxidation of ammonia in the presence of metallic alloys have also been hardly investigated. Presumably the same behaviour should apply here as in catalysis on the pure metals.

It has been shown[34] that the catalytic activity of the 90% Pt–10% Rh alloy increases when ammonia is oxidised by the O_2–O mixture instead of molecular oxygen. The homogeneous oxidation of NH_3 by atomic oxygen was ruled out[34] and it was assumed that acceleration is achieved either owing to the increase of the concentration of adsorbed oxygen or because excited activated species appear in the purely exothermic interaction of O atoms with the surface of the catalyst. The first hypothesis is consistent with schemes (VII)–(IX), because it follows from Eqn. (1) that the rate of reaction is proportional to θ.

3. Oxidation of Ammonia in the Presence of Simple Oxide Catalysts

Quantitative data on the catalytic properties of simple oxides in the oxidation of ammonia have been obtained in a number of studies[13,35,36] (Table 2). Under the conditions of these experiments, the reaction products were N_2 and N_2O and the process occurred in the kinetic region. The steady state was usually attained rapidly, in the course of 5–10 min. A phase transformation of the oxide (with the exception of Ag_2O) was not observed. Table 2 shows that at 230°C the specific catalytic activities of the oxides decrease in the following sequence:

$$Co_3O_4,\ MnO_2 > CuO > CaO_2 > NiO > Bi_2O_3 > Fe_2O_3 > V_2O_5 > TiO_2 > \\ > CdO > PbO > ZnO > SnO_2 > ZrO_2 > MoO_3 > WO_3$$

A similar sequence was obtained in another study[37], according to which the activities of the oxides decrease as follows:

$$Co_3O_4 > Mn_2O_3 > Cr_2O_3 > Fe_2O_3 > CuO > NiO > V_2O_5 > MoO_3 > U_3O_8 > \\ > ThO_2 > WO_3 > SnO_2 > ZrO_2 > ZnO > Nb_2O_5 > Bi_2O_3 > Sb_2O_4 > Ta_2O_5.$$

However, one should note that the activity of Bi_2O_3 observed by Germain and Perez[37] is significantly lower than that found by Il'chenko et al.[36]. According to other data[38,39], lanthanide (La, Ce, Pr) oxides exhibit a low activity in the oxidation of NH_3 and the activities of Al_2O_3 and SiO_2 are very low indeed. The activity of barium peroxide approaches that of Fe_2O_3.[40]

Thus, among the simple oxides, the highest activities in the oxidation of ammonia are shown by the transition metal oxides Co_3O_4, $MnO_2(Mn_2O_3)$, Cr_2O_3, and CuO, the oxides NiO, Fe_2O_3, and V_2O_5 are moderately active, and the activities of the oxides La_2O_3, Pr_6O_{11}, CeO_2, TiO_2, ZrO_2, ThO_2, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, and U_3O_8 are low. The oxides of elements in the main subgroups (except for calcium and barium peroxides) are relatively inactive. A similar behaviour has been observed in the oxidation of hydrogen[41,42], methane, benzene[41], and other inorganic and organic substances.

As in the presence of metals, the oxidation of ammonia in the presence of metal oxides results in the preferential formation of N_2 at low temperatures; on raising the reaction temperatures, nitrous oxide appears in the products, its yield passing through a maximum; at still higher temperatures (400–500°C and above), ammonia is oxidised to an even greater extent—to NO.[1,2,35-40] It has been noted[33] that, in the presence of each catalyst the temperature of the onset of formation of particular products increases in the sequence $N_2 < N_2O < NO$ (see Refs. 36, 38, 40 and Table 2).

At low temperatures and for low degrees of conversion, when only reactions (I) and (II) occur, the selectivity with respect to N_2O in the presence of the majority of oxides increases with temperature[36,40]. In this region, the selectivity with respect to N_2O falls in the sequence

$$CaO_2 > MnO_2,\ NiO > Co_3O_4 > Fe_2O_3 > SnO_2 > CdO > CuO >$$
$$> TiO_2 > ZnO,\ Bi_2O_3,\ PbO,\ ZrO_2,\ MoO_3,\ WO_3$$

(Table 2). Comparison of these data with other results[37,38] leads to the conclusion that the maximum selectivity with respect to N_2O (minimum selectivity with respect to N_2) is shown by the most active oxides (MnO_2, Mn_2O_3, Co_3O_4, CuO, NiO, Cu_2O, and CaO_2), so that the following tendency is observed: the selectivity with respect to mild oxidation varies in general in opposition to the catalytic activity, while the selectivity with respect to extensive oxidation varies in parallel with the activity[36].

Table 2. The oxidation of ammonia in the presence of metal oxides*.[13,35,36]

Catalyst	Specific surface, $m^2\ g^{-1}$	Sample, g	Temp. range of catalytic reaction, °C	$\lg r - 11$**	E, kcal mole^{-1}	S_{N_2O}, at 230°C, %	Temperature of onset of formation, °C	
							N_2	N_2O
Co_3O_4	5.25	11.25	130—170	2.35	22	38	130	140
MnO_2	24.60	3.625	110—160	2.35	18	43	110	120
CuO	0.92	10.79	220—260	1.60	23	11	220	230
CaO_2	3.20	8.56	200—260	0.54	15	50	<200	200
NiO	52.00	11.08	80—160	0.40	11	43****	80	105
Bi_2O_3	1.41	17.31	235—320	0.13	12	0	235	255
Fe_2O_3	22.10	6.72	220—270	0.07	24	17	220	230
V_2O_5	4.50	8.80	260—320	—0.16	26	0	260	—
TiO_2	5.71	8.23	265—320	—0.36	16	8****	265	290
CdO	10.4	16.45	205—275	—0.38	9	13	205	230
PbO	6.00	23.40	240—285	—0.64	16	0	240	260
ZnO	1.00	5.07	265—380	—0.79	31	0	265	295
SnO_2	2.53	15.69	210—260	—0.90	17	16	<210	210
ZrO_2	9.60	10.92	245—330	—0.91	18	0	245	>330
MoO_3	0.33	28.90	330—370	—1.50	33	0	330	—
WO_3	6.35	19.14	200—380	—2.22	22	0	200	>380
Ag_2O***	0 09	24.55	115—155	3.40	18	—	125	147

*Composition of reaction mixture: $p_{NH_3} = 0.1$ atm; $p_{O_2} = 0.9$ atm.

**r is the rate of the overall process (in mol.cm^{-2} s^{-1}) at 230°C.

***The oxide was reduced to the metal during the catalytic reaction.

****S_{N_2O} for NiO at 160°C and to TiO_2 at 290°C.

At high temperatures (700–800°C), reaction (III) proceeds at a high rate. Owing to the marked influence of macrokinetic factors, it is difficult to obtain rigorous quantitative selectivity data in this temperature range. Qualitative characteristics of the selectivity with respect to NO for various oxides at temperatures in the range 700–800°C have been published[43,44]. According to Kurin and Zakharov[43], the yield of NO decreases in the sequence

$$Co_3O_4 > MnO_2 > PbO > Cr_2O_3,\ Fe_2O_3 > CuO > NiO > ZnO >$$
$$> SnO_2,\ MoO_3,\ WO_3,\ TiO_2,\ Al_2O_3;$$

while Morozov et al.[44] obtained the sequence

$$Co_3O_4 > CuO > Cr_2O_3 > Fe_2O_3.$$

Thus, under these conditions too the selectivity with respect to the extensive oxidation products in general varies in parallel with the catalytic activity in relation to the overall process. The most active catalyst (among simple oxides), namely Co_3O_4, exhibits a fairly high selectivity with respect to N_2O at low temperatures and with respect to NO at high temperatures. This catalyst is sometimes used in practice in the oxidation of NH_3 to NO.[1]

The kinetics and mechanism of the oxidation of ammonia in the presence of oxide catalysts (Co_3O_4, MnO_2, CuO, Fe_2O_3, and V_2O_5; see Table 2) have been investigated[13,35,45,46]. The experiments were performed in a differential flow reactor (with conversions not exceeding 20%) and by the flow-circulation method. The reaction was studied at temperatures below 400°C when the products were N_2 and N_2O. The study of the variation of the rate of reactions (I) and (II) with contact time τ in the presence of the most active catalysts (Co_3O_4, MnO_2) showed that, under the chosen conditions, the values of r_i (and hence the selectivity) are independent of τ. This implies that reactions (I) and (II) take place simultaneously and are not inhibited by the products. The variation of the rate of the overall process and of specific reactions with p_{NH_3} and p_{O_2} is represented (for each catalyst) by hyperbolic curves: the reaction is of first order for low values of p_i, and of zero order for high values of p_i.

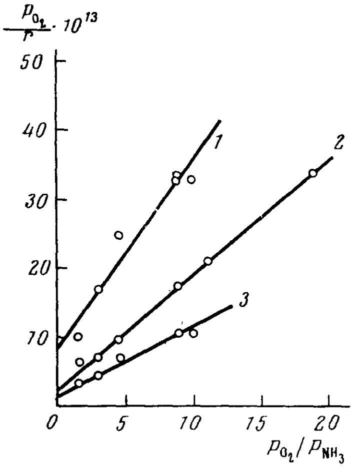

Figure 6. Variation of p_{O_2}/r with p_{O_2}/p_{NH_3} on an MnO_2 catalyst[13,46] at different temperatures (°C): 1) 135; 2) 145; 3) 155.

As in the catalytic reaction on platinum[4], mechanisms of the Langmuir–Hinshelwood type proved to be unsuitable for the interpretation of the experimental data. Scheme (VII) and the kinetic equations (1)–(4) corresponding to it proved to be the most appropriate. Figs. 6 and 7 show that these equations describe satisfactorily the experimental data for the MnO_2 catalyst. A similar result was obtained also for other oxides (Co_3O_4, CuO, Fe_2O_3, and V_2O_5). The rate constants, heats of activation, and entropies of activation for the first two stages of scheme (VII), calculated from the experimental data, have been compiled for the above catalysts[13]. The kinetic data[47] for the oxidation of ammonia in the presence of Cu_2O also agree with Eqns. (1)–(4).

The conclusion that S_{N_2O} increases with increase of θ agrees with the results of a study[40] where it was found that the yield of nitrous oxide increases with increasing concentration of the "excess" oxygen on the surface of transition metal oxides.

According to scheme (VII), the oxygen adsorption stage is irreversible. We shall now consider[45] another extreme case, where adsorption equilibrium is established in the first stage. If such a case does indeed occur, deviations from Eqn. (1) should be observed. The selectivity equations (3) and (4) retain their previous form, but the values of θ involved in them are determined by the oxygen adsorption isotherm and not by Eqn. (2). This means that, at a given temperature, the selectivity should be independent of p_{NH_3} and, for a constant p_{O_2}, it should remain unchanged; in reality, S_{N_2O} decreases with increase of p_{NH_3} (for p_{O_2} = const.), which corresponds to Eqn. (4).

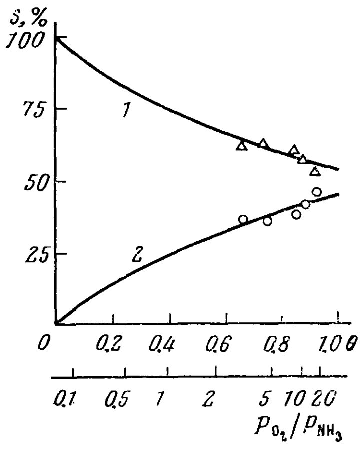

Figure 7. Variation of the selectivity with respect to N_2 (curve *1*) and N_2O (curve *2*) with p_{O_2}/p_{NH_3} and θ at 145°C on an MnO_2 catalyst[13,46] (μ = 1,2; k_1/k_2 = 0.55).

The similarity of the behaviour observed in the catalytic oxidation of ammonia and in the surface reduction of various oxides by ammonia (in the absence of O_2 from the gas phase) constitutes an independent demonstration of the involvement of the (O) species in the process and that their surface concentration θ plays a decisive role in the reaction kinetics. The following observations were made[13,35].

(1) The composition of the products in the catalytic and reduction reactions is the same (see the data of Krauss and Neuhaus[40]).

(2) The rate of the overall conversion of ammonia in the reduction process decreases with increase of the duration of reduction τ'. This result is consistent with Eqn. (1), since θ falls continuously as τ' increases. If the reduction is carried out after treating the catalyst with oxygen, whereupon the catalyst surface is fully oxidised in the initial state (θ is a maximum), then the initial rate of reduction is higher than the steady-state rate of the catalytic reaction. After a specific time τ', the rate of reduction becomes equal to the rate of the catalytic reaction; at this point, the values of θ for the catalytic and reduction reactions are the same. If the reduction is carried out immediately after the catalytic experiment, then the initial rate of reduction is close to the steady-state rate of the catalytic reaction.

(3) In conformity with Eqns. (3) and (4), the selectivity with respect to N_2 increases and that with respect to N_2O falls as τ' increases, i.e. as θ decreases.

The similarity of the characteristics of the catalytic oxidation of ammonia and of the surface reduction of oxides by ammonia shows that, in the interaction of NH_3 with the surface [the second stage in scheme (VII)], electrons are transferred from the ammonia molecule to the catalyst, i.e. NH_3 behaves as an electron donor. This is consistent with the results of studies[47,48] where the catalytic properties of oxides in the oxidation of ammonia were compared with their semiconductor properties.

It is natural to assume that the abstraction of hydrogen from the NH_3 molecule proceeds simultaneously with electron transfer from NH_3 to the catalyst and is completed gradually, in several stages: the formation of the final products from NH_3 and O_2 in a single stage would require the simultaneous collision of many species, which is unlikely. In order to demonstrate the involvement of (NH) and (HNO) species and possibly of other surface complexes in the process, it is necessary to employ physical research techniques. In this connection, we may note that the most probable product of the reaction between NH_3 and the surface oxygen of iron(III) oxide at low temperatures has been shown by infrared spectroscopy to consist of species of the nitroxyl type[49].

It has been shown by ESR[50] that, in the adsorption of ammonia at room temperature on partly reduced vanadium pentoxide deposited on silica gel, the NH_3 molecule enters into the first coordination sphere of the tetrahedrally coordinated V^{4+} ion. This results in a rearrangement of the coordination sphere and in the formation of a shortened vanadium–oxygen bond, characteristic of vanadyl ions. Thus formation of an unstable coordination compound may be the primary step in the activation of NH_3 during the catalytic process, facilitating the next electron transfer stage. This hypothesis appears probable, bearing in mind the tendency of transition metal cations to form complexes with ammonia, a molecule having a lone electron pair.

In the subsequent stages of the catalytic process, the (NH) and (HNO) species behave as electron donors, like ammonia. When these species are converted into the reaction products (N_2, N_2O, and H_2O), electrons are liberated. The reduced form of the catalyst cations M^{n+}_{red}, capable of giving up electrons, therefore corresponds to the free surface sites, appearing as a result of the fourth or fifth stages of scheme (VII).

In the adsorption of electron-accepting oxygen molecules on these centres, electrons combine with the O_2 molecules, forming negatively charged atomic ions (O) bound to the oxidised form of the cations M^{m+}_{ox}. Hence it follows that the surface concentration of the (O) species, equal to θ, is proportional to $[M^{m+}_{ox}]$, while the concentration of free sites ( ), equal to $1 - \theta$, is proportional to $[M^{n+}_{red}]$; the ratio of the concentrations of the oxidised and reduced forms $\gamma = [M^{m+}_{ox}]/[M^{n+}_{red}]$ will be proportional, under steady-stage conditions of the catalytic reaction, to $\theta/(1 - \theta)$. According to Eqn. (2), this implies that γ is proportional to p_{O_2}/p_{NH_3}, i.e. the degree of oxidation of the surface is determined by the ratio of the partial pressures of oxygen and ammonia in the reaction mixture.

The same quantity determines the catalytic selectivity (at a given temperature). The higher the value of p_{O_2}/p_{NH_3}, the higher the degree of surface coverage by oxygen θ. Since the activated complex in the stage leadng to the formation of N_2O incorporates a larger number of oxygen atoms than the activated complex in the stage leading to the formation of N_2 (see the fourth and fifth stages), an increase of p_{O_2}/p_{NH_3} tends to increase the selectivity with respect to the more oxidised product—nitrous oxide.

The kinetics and mechanism of the reaction in the presence of oxides at elevated temperatures have not been investigated. Presumably schemes of types (VIII) and (IX), taking into account the parallel-reaction oxidation of NH_3 to NO and the consecutive-reaction reduction of nitrous oxide by ammonia [here it is also necessary to take into account reactions (V) and (VI)], are valid for these conditions.

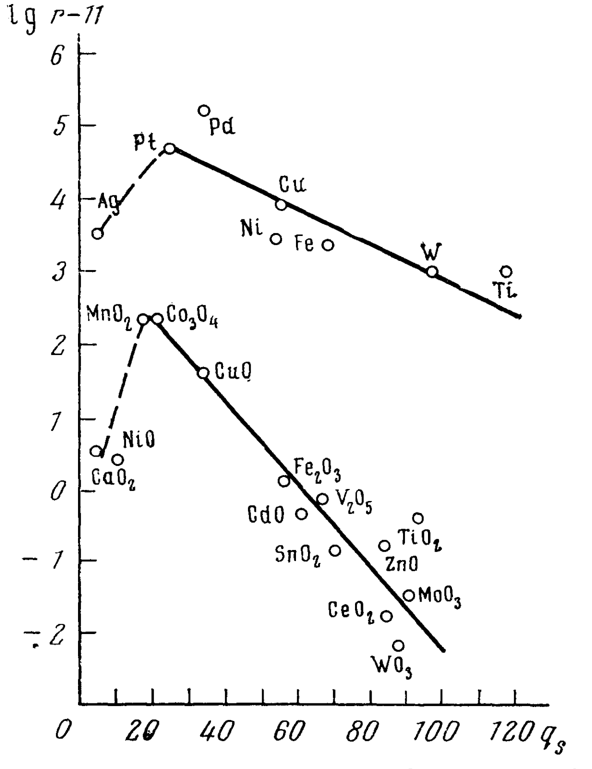

Figure 8. Variation of the specific catalytic activity of metals and oxides in the oxidation of NH_3 at 230°C with q_S; mixture composition: p_{NH_3} = 0.1 atm; p_{O_2} = 0.9 atm.[36]

The results of the theoretical analysis carried out above in relation to metallic catalysts (section II, subsection 1) can be usefully employed in the discussion of the problem of the relation between the catalytic and physicochemical properties of oxide catalysts. Such an examination, which has been carried out in a number of studies[27,28,36], is based on the hypothesis that the oxygen–catalyst bond energy q_S plays a decisive role. Arguments in support of this hypothesis have been obtained[36] by quantum-chemical calculations on complexes simulating the surface compounds of the oxidised and reduced forms of various oxide catalysts with oxygen and the NH species.

Fig. 8 shows that the correlation predicted by Eqn. (15) does indeed occur between q_S and the specific catalytic activity of the oxide. The correlation is analogous to that observed for transition metals. At the same time, it is seen that, under identical conditions, the absolute activity of metals exceeds considerably that of oxides[4,36]. The cause of the difference should probably be sought in the fact that, in the presence of transition metals, the preliminary activation of NH_3 molecules takes place on a metallic surface free from oxygen and leads to the dissociation (or considerable weakening) of the N–H bond (see section II, subsection 1); because of this, the absolute values of k_2 for metals are higher than for oxides[4]. Similar relations between the absolute catalytic activities of metals and oxides have been observed in the oxidation of hydrogen and certain organic substances[30].

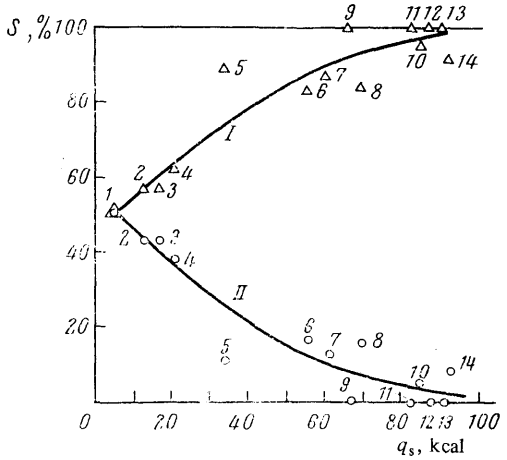

Figure 9. Dependence of the selectivity of oxides with respect to N_2 (curve *1*) and N_2O (curve *2*) on q_S at 230°C: 1) CaO_2; 2) NiO; 3) MnO_2; 4) Co_3O_4; 5) CuO; 6) Fe_2O_3; 7) CdO; 8) SnO_2; 9) V_2O_5; 10) CeO_2; 11) ZnO; 12) WO_3; 13) MoO_3; 14) TiO_2.[36]

Fig. 9 shows that the selectivity of the process with respect to N_2 increases with increase of q_S, while the selectivity with respect to N_2O falls. Such variation of selectivity follows from Eqns. (3), (4), (19), and (20). In addition to the above analysis, we shall consider[27,28] the variation of the rates of formation of N_2 and N_2O with q_S. It can be shown that, when $\theta \simeq 1$, we have

$$\rho_{N_2} = \frac{\partial \ln r_{N_2}}{\partial q_s} = -\frac{\alpha}{RT}\left(1 - \frac{\Delta n}{1+\mu}\right),$$

$$\rho_{N_2O} = \frac{\partial \ln r_{N_2O}}{\partial q_s} = -\frac{\alpha}{RT}\left(1 + \frac{\Delta n\mu}{1+\mu}\right).$$

It is readily seen that ρ_{N_2O} is negative like ρ [see Eqn. (17)]; the type of variation of the rate of extensive oxidation and of the overall rate of the process with q_S should therefore be qualitatively the same. The difference $\rho_{N_2O} - \rho_{N_2} = -\alpha\Delta n/RT$ is likewise negative, which implies that the rate of extensive oxidation should decrease with increase of q_S more rapidly than the rate of mild oxidation. Experiment confirmed this inference (Fig. 10).

The higher the value of q_S, the greater the contribution of r_{N_2} to the overall rate and the higher the selectivity with respect to the mild oxidation product (Fig. 9).

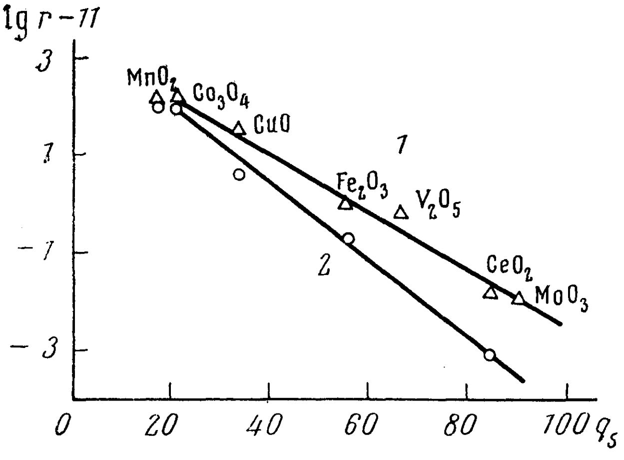

Figure 10. Variation of the rates of formation of N_2 (line 1) and N_2O (line 2) with q_S.[27]

This shows clearly that the principal cause of the increase of the selectivity with respect to the mild oxidation product with increase of q_S is that the formation of this product entails the dissociation of fewer oxygen–catalyst bonds than the formation of the extensive oxidation product[33].

When the above approach is extended to a more general case, where reactions (I)–(III) occur simultaneously, one may conclude that at high temperatures the selectivity with respect to NO should decrease with q_S. Fig. 11 shows that this inference is likewise fulfilled. The observed decrease with q_S of the catalytic activity in relation to the overall process and of the selectivity with respect to the extensive oxidation product explains the empirical observations noted above—the parallel variation of these quantities for a series of oxide catalysts.

The increase of the heats of activation in the sequence $E_{N_2} < E_{N_2O} < E_{NO}$ predicted by the theory[33] also agrees with experiment, since, in the presence of each oxide catalyst, the temperatures of the onset of formation of particular products increase in the sequence $N_2 < N_2O < NO$ (see Table 2 and the data in Refs. 36, 38, 40).

A correlation between the type of conductivity of the oxides and their catalytic properties in the ammonia oxidation reaction has been noted in a number of investigations[2,38,43]. The catalytic activity decreases in the sequence *p*-type semiconductors > *n*-type semiconductors > insulators; the selectivity with respect to N_2O (and NO) increases in the same sequence while that with respect to N_2 diminishes. The above correlation can be explained by the fact that there is a qualitative correspondence between the semiconductor properties of the oxides and the energy of the bond between oxygen and their surfaces[51]; *p*-type semiconductors (MnO_2, Co_3O_4, NiO, and CuO) have the smallest values of q_S, insulators (aluminium, silicon, and other oxides) are characterised by the highest values of q_S, while *n*-type semiconductors (V_2O_5, MoO_3, ZnO, TiO_3, etc.) occupy an intermediate position.

4. Oxidation of Ammonia in the Presence of Complex and Promoted Oxide Catalysts

Complex oxide catalysts based on MnO_2 exhibit a high activity in relation to the low-temperature oxidation of ammonia and at the same time a high selectivity with respect to N_2O. The temperature dependence of the yields of N_2, N_2O, and NO in the presence of these catalysts is of the same type as in the presence of simple oxide catalysts[1,2,40,52]. In the reaction involving the oxidation of NH_3 to N_2O at 200–300°C, MnO_2 with added Bi_2O_3 is extremely effective[2,39,53]. The studies discussed in the preceeding subsection showed that nickel(II) oxide is fairly active in relation to the overall reaction and selective with respect to the formation of N_2O. According to Giordano et al.[48], small amounts of lithium and sodium oxides added to this catalyst increase while added aluminium and iron oxides decrease the activity and selectivity, i.e., in this case, the activity and selectivity in relation to extensive oxidation vary in parallel.

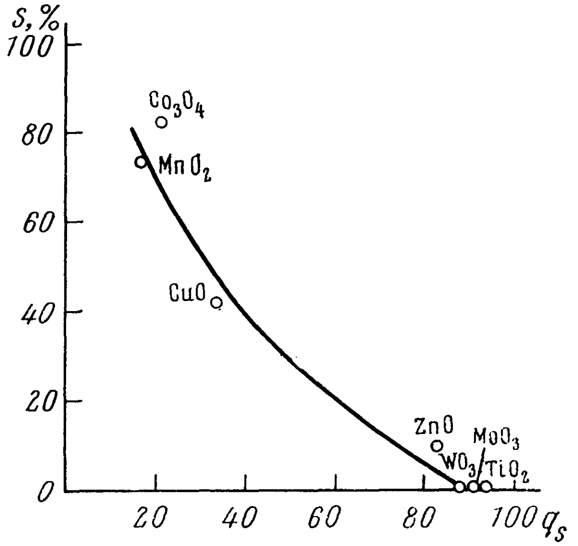

Figure 11. Dependence of the selectivity of oxides with respect to NO on q_S.[27]

In the high-temperature oxidation of ammonia, a high selectivity with respect to NO is shown mainly by complex catalysts, the chemical composition of which resembles that of the effective catalysts of the synthesis of N_2O at low temperatures. It has been shown[44] that, in the presence of cobalt oxide catalysts containing added copper, chromium, zinc, nickel, magnesium, iron, and silver oxides as well as copper and zinc chromites, the yield of NO attained at 700°C is 90–95%; best results are obtained in the presence of pure Co_3O_4. The 85% Co_3O_4–15% Al_2O_3 catalyst is sometimes used in practice[1]. In the presence of manganese oxide catalysts containing added chromium and copper oxides, the yield of NO is 60–80%.[44] The Fe_2O–MnO_2–Bi_2O_3 catalyst is fairly active (but is operation is unstable); complex iron oxide–chromium oxide catalysts are more stable and are used as the second component in two-component catalysts (platinum catalysts are used as the first component)[1].

In contrast to the catalysts based on Co_3O_4, MnO_2, and Fe_2O_3, accelerating the extensive oxidation of ammonia, which were discussed above, complex oxide catalysts based on MoO_3 catalyse, like MoO_3 itself, virtually only the mild oxidation of NH_3 (only to N_2).[54,55] Nitrogen oxides are obtained in very significant amounts in the presence of bismuth molybdate[54] and other molybdates[55]. The activity of such systems decreases in the sequence[55]

$$\text{Bi—Mo—O (Bi : Mo}=1) > \text{Fe—Mo—O} > \text{Mn—Mo—O} > \text{Co—Mo—O} >$$
$$> \text{Bi—Mo—O (Bi : Mo)} = 2) > MoO_3 > \text{Ca—Mo—O, Tl—Mo—O, Pb—Mo—O.}$$

The kinetics and mechanism of the oxidation of ammonia in the presence of complex oxide catalysts and the factors governing their selection have been little investigated. Nevertheless the isolated facts available suggest that this instance constitutes an analogy with catalysis by simple oxides:

(1) The kinetics of the overall process in the presence of MnO_2–Bi_2O_3 catalyst are said to be described[39] by the relation $r = kp_{NH_3}\theta$, i.e. Eqn. (1).

(2) In the presence of complex catalysts, the same relations are observed between the temperatures of the onset of the formation of N_2, N_2O, and NO as in the presence of simple oxide catalysts.

(3) The qualitative composition of the products in the surface reduction of complex oxides by ammonia and in the catalytic reaction is the same[40,55], as for simple oxides.

(4) Since complex catalysts based on Co_3O_4 and MnO_2 have a much lower oxygen binding energy than the catalysts based on MoO_3, presumably the same relations between q_S and the activity and selectivity are valid qualitatively for complex catalysts as for simple oxides: the first group of catalysts (based on Co_3O_4 and MnO_2) are active and selective in relation to the extensive oxidation of ammonia, while the activity of the second group (based on MoO_3) is low, but the catalysts are selective in relation to the mild oxidation. The validity of relations of this kind for complex oxide catalysts too provides a natural explanation of the opposite variation of r and S_{N_2} observed for such catalysts.

Thus, by altering the oxygen–oxide catalyst bond energy as a result of the introduction of additives, it is possible to regulate the activity and selectivity of the catalyst in the oxidation of ammonia.

A fundamentally new method for the selection of a low-temperature catalyst for the synthesis of nitrous oxide from ammonia was used by the present author[19]. The idea is as follows. Since we have seen that a high selectivity with respect to N_2O is achieved on oxides with low values of q_S, oxides such as MnO_2 and Co_3O_4 can be used as a basis for the above catalyst. Next, it is necessary to increase the activity of these without altering q_S, since otherwise the selectivity would fall. Such a method of increasing the activity is provided by the dissimilarity (noted above) of transition metals and their oxides, associated with the higher rate of activation of ammonia on metallic surfaces. When small amounts of platinum or palladium are introduced into the oxide, then q_S for the oxide remains unchanged, but the rate of oxidation of ammonia should increase owing to its activation on the metal. Using this procedure, it was indeed possible to obtain new extremely active and selective catalysts for the oxidation of NH_3 to N_2O (cobalt or manganese oxide promoted by platinum). In the presence of these catalysts at low temperatures (of the order of 200°C), ammonia can be fully converted, the selectivity with respect to N_2O being 60–80%.[19]

The study of the reaction kinetics in the presence of the above promoted catalysts showed that the same Eqns. (1) to (4) are valid for them as for the unpromoted oxides. This demonstrates that the introduction of additives does not cause a fundamental change in the reaction mechanism but there is an appreciable increase of the rate of reaction of ammonia with the surface oxygen of the oxide. This is proved by the observed acceleration of the surface reduction of cobalt and manganese oxides by ammonia in the presence of small amounts of added platinum[19].

A similar promotion effect was demonstrated previously in the oxidation of hydrogen on vanadium pentoxide[56]. We may note that the reactivity of ammonia in its oxidation on metal oxides is close to the reactivity of molecular hydrogen[36].

5. Oxidation of Ammonia on Zeolites Containing Transition Metals

The oxidation of ammonia on a type Y zeolite containing Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, and Ag^+ cations has been investigated[57] by a pulse method ($O_2 : NH_3 = 3 : 1$). The cations were introduced into the initial NaY zeolite by ion exchange from solutions of the metal nitrates. The degree of exchange (%) was 70.5 for CuY, 50.0 for FeY, 55 for CoY, 80.4 for CrY, 48.0 for NiY, 56 for MnY, and 51.7 for AgY. After the exchange, the colour of the zeolite corresponded to the colour of the cations in the aqueous solution. The aluminosilicate crystal structure of the NaY specimen was retained in the exchange reaction. It also remained unchanged after the specimens had been heat-treated at temperatures up to 600°C. The only exception was the chromium catalyst in which the formation of a α-Al_2O_3–Cr_2O_3 solid solution was observed.

The catalytic activity was characterised by the degree of conversion of ammonia for the same weight of the metal in the zeolite. The following activity series was established:

$$\text{CuY} > \text{CrY} > \text{AgY} > \text{CoY} > \text{FeY} > \text{NiY, MnY.}$$

The reaction product was molecular nitrogen in the presence of all the above catalysts. A fairly small amount of nitrous oxide was also formed in the presence of the chromium- and silver-zeolites; in the presence of AgY, the selectivity with respect to N_2O at 400°C was approximately 25%. On other zeolites, the selectivity with respect to this product was 1–5%. The authors[57] believe that the process proceeds via a parallel-consecutive reaction mechanism, the N_2O formed being converted into N_2 via reaction (IV). A high rate of this reaction at the temperatures of the catalytic oxidation of ammonia has been demonstrated for the CuY catalyst.

The study of the alternate oxidation of the catalysts by oxygen pulses and of the reduction of the oxidised specimen by ammonia showed that N_2 is formed on reduction in the presence of the FeY, CuY, and CrY zeolites, which absorb O_2; the MnY and CoY catalysts do not absorb oxygen. The adsorption of ammonia on the CuY catalyst at room temperature leads to a change in the colour of the latter, which becomes blue, i.e. is characteristic of the coordination compounds of NH_3 and Cu^{2+}. There is a simultaneous change in the ESR spectrum of the specimen. The adsorbed ammonia is removed by evacuation (at 60°C), whereupon the specimen returns to the initial state. The adsorption of O_2 at 385°C does not change the ESR spectrum of the zeolite. When ammonia is readmitted at 385°C, some of the Cu^{2+} ions are reduced; the copper atoms formed can be reoxidised by oxygen.

A different behaviour is observed in the presence of the MnY zeolite: the ESR spectrum changes only when NH_3 is adsorbed at room temperature. The retention of the ESR signal following the interaction of the zeolite with O_2 and NH_3 at elevated temperatures suggests that in this case the valence state of the manganese in the zeolite remains unaltered. X-Ray diffraction studies of all the zeolites after exposure to a stream of ammonia at 500°C failed to reveal any changes relative to the initial state, which indicates the absence of a metallic phase.

Comparison of the metal cations shows that the above zeolite activity series differs significantly from the corresponding series obtained for oxide catalysts (see subsection 3 of this section). This is evidently associated with the fact that the intermediate chemical interaction in the catalytic process on the zeolite is of the local type and involves a single catalyst cation, while in catalysis on solid oxides collective interactions due to the presence of the crystal lattice also play a significant role.

The authors[57] suggest that a mechanism involving the alternate reduction and oxidation of the catalyst cations is possible on the CuY and FeY zeolites, while in the presence of the MnY, CoY, and NiY zeolites, where the valence state of the metal is stabilised, a mechanism involving the simultaneous interaction of the catalyst with NH_3 and O_2 is probable.

III. THE ANALOGY BETWEEN THE SELECTIVE OXIDATION REACTIONS OF AMMONIA AND ORGANIC SUBSTANCES[27,28]

The oxidation of ammonia is a convenient reaction for the elucidation of the general characteristics of selective catalytic oxidation. In many significant respects, the mechanism of this reaction is similar to that of the oxidation of organic substances. The similarity is manifested in the kinetics. Thus the kinetic equations for the overall oxidation of *o*-xylene[58] and ammonia are analogous. In the oxidation of *o*-xylene[58], but-1-ene[59], and other substances (R), the selectivity with respect to the mild oxidation product increases with increase of the ratio p_R/p_{O_2} in the reaction mixture, as has been observed in the oxidation of NH_3, where the selectivity with respect to nitrogen increases with p_R/p_{O_2}.

The catalytic activity in the oxidation of both ammonia and organic substances is determined primarily by the energy of the bond formed by oxygen with the catalyst surface, the optimum corresponding to low values of q_S. The similarity of the mechanisms of these reactions is responsible for the analogous variation of the catalytic activity as a function of q_S. This explains the finding that the most active catalysts for the oxidation of NH_3 and organic substances are the same (Co_3O_4, MnO_2, and platinum).

The general rule whereby one can understand the nature of the variation of selectivity as a function of q_S is that the formation of the extensive oxidation products (CO and CO_2 in the oxidation of organic substances and N_2O and NO in the oxidation of ammonia) involves the dissociation of a larger number of oxygen–catalyst bonds than the formation of the mild oxidation products (aldehydes, ketones, etc. in organic catalysis and N_2 in the oxidation of NH_3). As a result of this, the selectivity with respect to the mild oxidation products increases and that with respect to the extensive oxidation products decreases with increase of q_S. This implies that a high selectivity with respect to the extensive oxidation products is attained on catalysts with low values of q_S, in agreement with the condition for the highest activity of the catalyst, and explains why the best catalysts for the oxidation of NH_3 to NO and for the complete combustion of organic substances are usually Co_3O_4 and platinum.

Experiments have shown that the optimum values of q_S for the mild oxidation reactions of organic substances is close to the value of q_S for V_2O_5 and for complex catalysts based on V_2O_5 and MoO_3, because the latter are used to accelerate these reactions. The similarity of the mild oxidation reactions of organic substances and ammonia is manifested by the fact that the same catalysts are used also in the mild oxidation of NH_3.

There are also definite differences between the oxidation reactions of organic substances and ammonia. These involve primarily the thermodynamics of the reactions. In the oxidation of organic substances, the extensive oxidation products are thermodynamically more stable than the mild oxidation products, while in the oxidation of ammonia the opposite behaviour is observed (see Section I). In the former case, the mild oxidation product is desired and in the latter the aim is to obtain the extensive oxidation product. This is reasonable, since the advantage of catalysis are reflected in the possibility of obtaining thermodynamically less stable products. The above feature of the thermodynamics of the reactions compared is manifested by the finding that, in the oxidation of ammonia (in contrast to the oxidation of organic substances), an enhanced rate of formation of the mild oxidation product and a reduced observed rate of extensive oxidation correspond to the consecutive reaction scheme.

One must note that the approach used above to establish a relation between the catalytic properties and chemical structures of substances has certain limitations. In a more rigorous treatment, it is necessary to take into account the energy inhomogeneity of the surface oxygen[60], which can play the same role on a given catalyst as the changes in the oxygen binding energy on passing from one catalyst to another. Another simplification is associated with the hypothesis that only the energy of the oxygen–catalyst bond changes significantly from one catalyst to another. In a more exact analysis, one must take into account also the changes in the energies of other bonds formed with the catalyst[32]. Allowance for the energies of other bonds should be understood in a fairly broad sense, including the formation of coordination compounds via π bonding, etc. as well as salt-like surface complexes. In the latter case, the acid–base properties of the catalyst play a significant role[61]. One can also suppose that, in the oxidation of complex organic molecules, the geometrical factor should have a definite importance (the requirement for multipoint adsorption).

It follows from the results discussed that, in the oxidation of ammonia, the acid–base and other properties of the catalysts play an appreciably smaller role than in the oxidation of organic substances, so that the decisive importance of the energy of the bond between oxygen and the surface is shown much more distinctly. In this respect, the oxidation of ammonia is closer to the oxidation reactions of inorganic molecules such as H_2 or CO_2.

IV. CONCLUSION

The analysis carried out in this review has shown that the kinetic method combined with physical research techniques can be employed to establish important features of the mechanism of the oxidation of ammonia under conditions where the oxidation products are nitrogen and nitrous oxide. It follows from the available data that the mechanism is qualitatively similar for metallic and oxide catalysts. The observed differences are largely quantitative and are caused by the specific features of the interaction of the oxidised molecule with the metallic surface. The mechanisms examined, considered in conjunction with the Brønsted–Temkin relation, serve as a fruitful basis for the determination of a relation between the thermodynamic properties of substances and their activities and selectivities in the oxidation of ammonia.

At the same time, one should note many unsolved problems, which include the kinetics and mechanism of the reaction at high temperatures, where NO is formed, the catalytic properties of complex catalysts in the kinetic region, the nature of the intermediate chemical interaction at elevated temperatures, and the role of homogeneous stages in the mechanism of the oxidation of ammonia. The solution of these problems will accelerate progress in the practical selection of new effective catalysts for this most important catalytic reaction.

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Organometallic Peroxy-compounds and Their Reactions

G.A.Razuvaev and T.G.Brilkina

Experimental studies on the synthesis and reactions of organometallic peroxy-compounds are reviewed and the reactions of organometallic compounds with oxygen and organic peroxides, leading to the formation of both peroxide and non-peroxide products, are considered. The possible modes and mechanisms of the chemical reactions of organometallic peroxy-compounds are discussed.

The bibliography includes 274 references.

CONTENTS

I. INTRODUCTION

The advances in the chemistry of organic peroxides have been recently widely described in numerous reviews and monographs and have been discussed at All-Union and International Conferences. On the other hand, the problem of the synthesis of organometallic peroxy-compounds (OMPS) and their chemical reactions have so far been little investigated, although these compounds are of undoubted interest both as regards theoretical research and for practical applications. Much attention has been devoted to these problems at the Gorky Institute of Chemistry from different standpoints: systematic research is being carried out on the synthesis and reactions of OMPS and their role in the autoxidation of organometallic compounds (OMC), the mechanisms of the reactions of OMC with various peroxides are being investigated, and the initiating capacity of OMPC and OMC–oxygen and OMC–peroxide systems in free-radical processes are being elucidated.

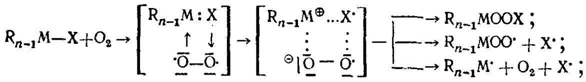
It is useful to examine the fundamental trends in such research, resorting where necessary to data of other investigators. The review does not include information about the peroxy-compounds of boron, phosphorus, and transition metals. There is an extensive literature on these compounds, the consideration of which is impossible within the framework of this article. For boron (R_3B) and phosphorus (R_3P and R_5P) compounds, only the results of a few studies are quoted, confirming the mechanisms of the reactions of their chemical analogues. Attention is concentrated in the review on studies carried out in recent years.

II. REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH OXYGEN AND PEROXY-COMPOUNDS

Many OMC are oxidised by atmospheric oxygen with formation of peroxy-compounds. This process is used as a method of synthesising organic hydroperoxides with primary and secondary organic groups (for example, the oxidation of magnesium and aluminium compounds in ether at a low temperature followed by the hydrolysis of the resulting OMPC). In order to obtain the OMPC in a pure form, the autoxidation of the OMC is not usually employed, since the process is accompanied by secondary molecular and radical reactions of the peroxides.

Some OMC, for example compounds of Group I–III elements, are known to interact readily with oxygen, while others are oxidised only under severe conditions (derivatives of Group IVB elements). Aryl OMC are more resistant to oxygen than the alkyl derivatives. The length and structure of the organic group attached to the metal, the presence of functional groups, etc., are important[1-3]. The oxidation of OMC by oxygen is a complex chemical process. It has now been shown convincingly[4] that the primary reaction in the autoxidation of many OMC is their bimolecular reaction with oxygen. Compounds of Group I–III elements as well as many compounds having an M–M bond react in this way. On the other hand, the autoxidation of the OMC of Group IVB elements[5-7] is initiated by the radicals formed in the spontaneous decomposition of the OMC in the initial stage.

The molecular interaction of OMC with oxygen (or ozone) involves several successive microstages: the coordination of oxygen (or ozone) to the central atom of the OMC via the oxygen p-electrons and the vacant atomic orbitals of the heteroatom and electrophilic attack by the coordinated oxygen on the M–C or M–M bonds followed by electron transfer leading to the formation of either an OMPC or of organic, organometallic, or peroxy-radicals[4,8-12]:

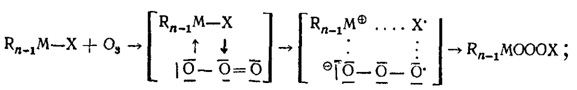


$$R_{n-1}M{-}X + O_2 \rightarrow \begin{bmatrix} R_{n-1}M : X \\ \uparrow \ \downarrow \\ \cdot\underline{\overline{O}}{-}\underline{\overline{O}}\cdot \end{bmatrix} \rightarrow \begin{bmatrix} R_{n-1}M^{\oplus} \ldots X^{\cdot} \\ \vdots \qquad \vdots \\ {}^{\ominus}|\underline{\overline{O}} - \underline{\overline{O}}\cdot \end{bmatrix} - \begin{cases} \longrightarrow R_{n-1}MOOX; & (1) \\ \longrightarrow R_{n-1}MOO^{\cdot} + X^{\cdot}; & (2) \\ \longrightarrow R_{n-1}M^{\cdot} + O_2 + X^{\cdot}; & (3) \end{cases}$$

$X{=}R$, $E'R_m$, $E''(MR_{n-1})_m$;

$M{=}$Li, Mg, Zn, Cd, B, Al, Tl, Si Ge, Sn, or Pb;

E' and $E''{=}$Hg, or Sb



$$R_{n-1}M{-}X + O_3 \rightarrow \begin{bmatrix} R_{n-1}M{-}X \\ \uparrow \ \downarrow \\ |\underline{\overline{O}} - \underline{\overline{O}} = \underline{\overline{O}} \end{bmatrix} \rightarrow \begin{bmatrix} R_{n-1}M^{\oplus} \ \ldots\ldots \ X^{\cdot} \\ \vdots \qquad\qquad \vdots \\ {}^{\ominus}|\underline{\overline{O}} - \underline{\overline{O}} - \underline{\overline{O}}\cdot \end{bmatrix} \rightarrow R_{n-1}MOOOX; \quad (4)$$

$X{=}R$, MR_m, or H; $M{=}$Si, Ge, Sn, or Pb.

The high electron affinity of ozone is responsible for the formation of a reactive OMC–ozone complex by compounds which do not enter into similar reaction with oxygen under the usual conditions. The oxidation by ozone of organic derivatives of Group IVB elements, metal alkyls, dimetal hexa-alkyls, halogen-containing derivatives of tin and lead, trisubstituted organosilanes, and other compounds proceeds at a low temperature (between room temperature and −68° or even −100°C [13−27]).

The OMPC formed via reaction (1) can react under autoxidation conditions with the initial OMC, yielding an alkoxy-derivative or decomposing into radicals with dissociation of O−O or M−O bonds:

$$R_{n-1}MOOR + R_{n-1}MR \rightarrow 2R_{n-1}MOR\ ; \qquad (5)$$

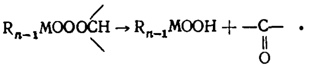
$$R_{n-1}MOOR \rightarrow R_{n-1}MO^{\cdot} + {}^{\cdot}OR\ ; \qquad (6)$$

$$R_{n-1}MOOR \rightarrow R_{n-1}M^{\cdot} + {}^{\cdot}OOR\ . \qquad (7)$$

The radicals formed in the decomposition of the OMC−oxygen complex [Eqns. (2) and (3)] and in the decomposition of the peroxide [Eqns. (5)−(7)] enter into the usual radical reactions in the cage or in the bulk of the solvent. At advanced stages of the autoxidation process, the homolytic substitution of the organic group in the OMC by the peroxy-radical is a very important reaction among these transformations:

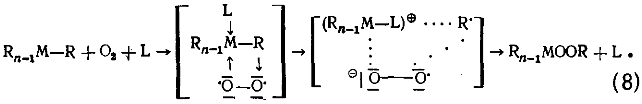
$$ROO^{\cdot} + R_nM \rightarrow R_{n-1}MOOR + R^{\cdot}\ .$$

The trioxide formed via reaction (4), in which X is a primary or secondary alkyl group, decomposes to an OMPC and a carbonyl compound:



$$R_{n-1}MOOO\!\!<\!\!CH \rightarrow R_{n-1}MOOH + \underset{\displaystyle \overset{\|}{O}}{-C-}\ .$$

The bimolecular interaction of an OMC with oxygen or ozone [Eqns. (1) and (4)] is very strongly influenced by the specific solvation of the OMC. The reaction may be catalysed by the introduction of a ligand L, which makes the metal more nucleophilic:



$$R_{n-1}M{-}R + O_2 + L \rightarrow \left[\begin{array}{c} L \\ \downarrow \\ R_{n-1}M{-}R \\ \uparrow \quad \downarrow \\ {}^{\cdot}\bar{\underline{O}}{-}\bar{\underline{O}}{}^{\cdot} \end{array}\right] \rightarrow \left[\begin{array}{ccc} (R_{n-1}M{-}L)^{\oplus} & \cdots\cdots & R^{\cdot} \\ \vdots & & \cdot \\ {}^{\ominus}|\bar{\underline{O}} & \text{——} & \bar{\underline{O}}{}^{\cdot} \end{array}\right] \rightarrow R_{n-1}MOOR + L\ . \qquad (8)$$

When the entire coordination capacity of the OMC is saturated by the ligand species, the coordination of O_2 or O_3 to the heteratom becomes impossible and the OMC exhibits an enhanced resistance to oxidation.

The formation of free radicals in the autoxidation of OMC has been demonstrated by employing labelled compounds (using ^{14}C and D). For example, the oxidation of PhLi and phenyl derivatives R_2M (M = Mg, Zn, or Cd) in labelled benzene proceeds with participation of Ph radicals, which react with the solvent and give rise to half-labelled biphenyl. The phenol isolated from the hydrolysis products in the reaction mixture is formed solely from the OMC.[28−32] The reactions of Ph radicals with other solvents (cyclohexane, chloroform, and carbon tetrachloride) [32−35] and the accelerating effect of additives (ethers) [28, 36−39] have also been noted.

In contrast to Ph_2Cd, whose oxidation proceeds wholly via a free-radical mechanism[35], the reaction of Et_2Cd with oxygen (in n-heptane at −80°C) proceeds without the participation of free radicals. This was confirmed by the autoxidation of Et_2Cd in the presence of effective inhibitors (*o*-phenylenediamine, galvinoxyl, and phenothiazine), used previously to demonstrate the free-radical mechanism of the oxidation of dimethylcadmium and organoboron compounds[40]. In the autoxidation of Et_2Cd in heptane, the reversible formation of an OMC−oxygen complex, which is comparatively stable in solution and is subsequently converted into a peroxy-product, was demonstrated experimentally for the first time[41]:

$$Et_2Cd + 2O_2 \rightleftarrows Et_2Cd \cdot 2O_2\ ;$$

$$Et_2Cd \cdot 2O_2 \rightarrow (EtOO)_2Cd\ .$$

The diethylcadmium−oxygen complex is formed over a wide temperature range (between −80° and 20°C). Its slow conversion into the ethylperoxy-derivative of cadmium can be observed even at room temperature. Substances containing atoms with electron-donating properties catalyse the reversible conversion of the complex into a peroxy-compound.

The replacement of one Ph-group in Ph_2Zn or Ph_2Cd by a Ph_3SiO group has a marked influence on the behaviour of the heterosiloxanes $PhMOSiPh_3$ (M = Zn or Cd) towards oxygen. For example, $PhZnOSiPh_3$ [42] and $PhCdOSiPh_3$ [43] are hardly oxidised by molecular oxygen under the usual conditions; the behaviour of $CH_3CdOSiPh_3$ is the same[43]. The alkyl derivative $EtZnOSiPh_3$ slowly absorbs oxygen but is nevertheless more resistant to O_2 than dialkyl- and diphenyl-zinc. On the other hand, $EtCdOSiPh_3$ is oxidised readily in benzene at room temperature, the organocadmium peroxide being formed in 92% yield[43]:

$$EtCdOSiPh_3 + O_2 \rightarrow EtOOCdOSiPh_3\ .$$

Primary alkyl compounds of mercury (Et_2Hg and n-Pr_2Hg) are resistant to oxygen. On the other hand, compounds with secondary (cyclohexyl and isopropyl) and tertiary (t-pentyl) groups undergo autoxidation via a free-radical mechanism including the bimolecular interaction of the OMC with oxygen in the initial stage [Eqn. (1)] and the formation of an unstable peroxide, which reacts further in accordance with Eqns. (5) and (7).[33,44−51]

Alkylperoxy-radicals $RO_2^{\cdot}$ behave as oxidants:

$$RO_2^{\cdot} + R_2Hg \rightarrow ROH + R_{-H}{=}O + RHg^{\cdot}\ .$$

The $RHg^{\cdot}$ radicals, formed both in the initial stage and at advanced stages of the process as a result of the decomposition of RHgOR,[44,52] decompose in their turn into mercury and the alkyl radical or are oxidised to peroxy-radicals[33,44]:

$$RHg^{\cdot} \rightarrow R^{\cdot} + Hg\ ;$$

$$RHg^{\cdot} + O_2 \rightarrow RHgOO^{\cdot}\ .$$

Like the $RO_2^{\cdot}$ radicals, the latter oxidise the OMC with formation of the final products:

$$RHgO_2^{\cdot} + R_2Hg \rightarrow RHgOR + RHgO^{\cdot}\ .$$

The alkoxy-derivatives of mercury thus formed react with oxygen more readily than the initial R_2Hg, but also in accordance with the free-radical chain mechanism[52].

Dicyclohexylmercury is oxidised by air at an appreciable rate even at room temperature. The main oxidation products in isopropyl alcohol at 60°C are cyclohexanol, cyclohexanone, and metallic mercury[49]. The oxidation products of i-Pr_2Hg in cyclohexane, cyclohexene, and benzene at 50°C are mercury, isopropylmercury isopropoxide, isopropylmercury hydroxide, acetone, isopropyl alcohol, propane, and propene. Apart from the above compounds, small amounts (approximately 5%) of phenyl derivatives have been detected in benzene, namely isopropylphenylmercury, Ph_2Hg, biphenyl, and isopropylbenzene[48]. Solvent involvement has been confirmed by isotopic and mass-spectrometric methods using in the oxidation reaction $(CH_3)_2CHOD$, $(CH_3)_2CDOH$, and isopropyl alcohol or R_2Hg labelled with ^{14}C.[45] The formation of free radicals in the autoxidation of R_2Hg [48−50] has been confirmed experimentally also by the inhibitor method[33,44].

Organoboron compounds are known to be readily oxidised by oxygen with formation of a large number of different products, the proportions of which depend very markedly on the reaction temperature and the solvent. It is suggested[3] that the primary R_3B–oxygen molecular complex is converted into a more or less stable organoboron peroxide in accordance with Eqn.(1). The peroxide is then converted into an alkoxy-derivative in accordance with Eqn.(5) or decomposes with formation of free radicals.

The oxidation of organoaluminium compounds proceeds in the main similarly to the oxidation of boron alkyls. The formation of organoaluminium peroxide was demonstrated for the first time by Sladkov et al.[53] and then confirmed by the low-temperature oxidation of Et_3Al.[54–56] The primary stage of the process is reaction (1). The subsequent interaction of the peroxide with the unoxidised OMC in accordance with Eqn.(5) leads to the formation of the corresponding aluminium alkoxides—the main oxidation products of R_3Al at a moderate temperature. Thus the yield of the peroxy-compound in the oxidation of Et_3Al by dry air in n-heptane at temperatures between −75° and 25°C is higher the lower the initial concentration of Et_3Al and the lower the reaction temperature. In a few instances, the yield of peroxide reaches 50%. At 25°C the peroxide is not detected in the reaction products[55]. As for boron alkyls, there is a succession of stages in the oxidation of the C–Al bond, the rate of oxidation varying appreciably with the number of oxidised alkyl groups. For example, in heptane (at 20–50°C) the ratios of the rates of oxidation of Et_3Al, Et_2AlOEt, and $Et(EtO)_2Al$ are 100 : 25 : 1.[56] Although $Et_3(EtO)Al$ is also oxidised at a high rate, on complete oxidation of Et_3Al under these conditions the yield of $(EtO)_2AlEt$ is low, since the compound exchanges radicals with the initial OMC. This reaction is rapid even at 5–10°C:

$$Et_3Al + (EtO)_2AlEt \rightarrow 2\,Et_2AlOEt\ .$$

In the oxidation of Et_2AlBr (between −30° and 30°C), such exchange does not occur and the reaction is accompanied by the formation of $(EtO)_2AlBr$ only[56].

Ph_3Al is oxidised in benzene, n-hexane, n-nonane, and ethyl ether more slowly and the solvent is involved in the oxidation[30,57,58]. Thus phenol (after hydrolysis) and biphenyl were found in the oxidation of Ph_3Al in benzene, and phenol, acetophenone, acetaldehyde, and alumina were found after the reaction in ether.

Et_3Tl is oxidised without the formation of free radicals. The peroxide produced via reaction (1) shows a smaller capacity for decomposition and isomeric transformations than the aluminium analogue. It was therefore possible to obtain the peroxide $Et_2TlOOEt$ in the oxidation of Et_2Tl in n-octane at −70°C.[59]

The organic compounds R_4M (where M = Si, Ge, Sn, or Pb, and R = alkyl) are in most cases highly resistant to oxygen. They react appreciably with oxygen at a fairly high temperature. The primary reaction in the autoxidation of such OMC as well as symmetrical organobimetallic compounds R_3M–MR_3 is homolytic decomposition of the initial compound at the metal–carbon or metal–metal bond, for example:

$$Et_4M \rightarrow Et_3M^{\bullet} + Et^{\bullet}\ ;$$
$$Et_3M\text{—}MEt_3 \rightarrow 2\,Et_3M^{\bullet}\ (\text{or}\ \ Et_3M\text{—}\dot{M}Et_2 + Et^{\bullet})\ ;$$
$$M{=}Sn,\ \text{or}\ Pb.$$

The development of the free radical chain process is due to the formation and further interactions of the peroxy-radicals:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}\ ;$$
$$R{=}Et,\ Et_3Sn,\ \text{or}\ Et_3Pb\ .$$

In the case of Et_4Pb (80–130°C, without solvent or in alkanes), degenerate chain branching by the peroxy-product and a number of other side reactions of the latter take place in addition to the reactions of the $RO_2^{\bullet}$ radicals with the initial OMC and their decomposition reactions[6,7,60–62]:

$$EtO_2^{\bullet} + Et_4Pb \rightarrow Et_3PbOOEt + Et^{\bullet}\ ;$$
$$Et_3PbOO^{\bullet} \rightarrow Et_2PbO + EtO^{\bullet}\ .$$

A characteristic feature of the autoxidation of Et_6Sn_2 (60–90°C, without solvent or in alkanes) is the absence of degenerate branching, owing to the high reactivity of the peroxy-compound with respect to the initial OMC:[60,61,63,64]

$$RO_2^{\bullet} + Et_3SnSnEt_3 \rightarrow Et_3SnOOSnEt_3 + R^{\bullet}\ ;$$
$$Et_3SnOOSnEt_3 + Et_3SnSnEt_3 \rightarrow 2\,Et_3SnOSnEt_3\ ,$$
$$RO_2^{\bullet} \rightarrow \text{products}\ ,$$
$$R{=}Et,\ \text{or}\ Et_3Sn\ .$$

The formation of the peroxide in small amounts in the oxidation of Et_6Sn_2 has been demonstrated by infrared spectroscopy[63].

The autoxidation of Et_6Pb_2 (40–90°C, without solvent, in hydrocarbons, or in Et_4Pb) proceeds in the initial stages similarly to the oxidation of Et_6Sn_2 with the preferential dissociation of the Pb–Pb bond[60,61,63–65]. The kinetic process characteristics are more complex, since, as the process proceeds, "limiting" behaviour due to the influence of the reaction products is observed. Nor can one rule out the role of steric factors. For example, the latter explains the higher reactivity of Ph_6Pb_2 with respect to t-$BuO_2^{\bullet}$ radicals compared with that of Ph_6Sn_2.[66]

The photoinitiated oxidation of the compounds R_4M (M = Sn or Pb) with the same and different alkyl groups[67–69] as well as the oxidation of $(Et_3Sn)_2O$[70] proceeds comparatively rapidly at room temperature, while Et_6Sn_2 is oxidised[71] even at temperatures in the range between −30° and 0°C. In the free-radical chain process involving the conversion into peroxy-radicals of the radical pairs formed in the photolysis of the M–C or M–M bonds, there is competition with the photosensitised oxidation of the OMC, the primary product of which is the corresponding OMPC. In many cases, the yield of peroxide reaches 15–25%.[68,69] The radicals are formed as a result of the photochemical dwcomposition of the peroxides at the O–O bond.

An increase of reactivity of the OMC of Group IVB metals towards oxygen is observed when the organic group in R_4M is replaced by groups derived from organic derivatives of the elements of the type EMR_3, where E is an element of Group II or V.[7,61,64,65,72,73] The reactions of such compounds with oxygen proceed under very mild conditions via a bimolecular mechanism without the participation of free radicals[74–79]. Dimetalloxanes are formed in accordance with Eqns.(1) and (5), for example:

$$\begin{gathered}(R_3M)_2Hg + O_2 \rightarrow R_3MHgOOMR_3\ ;\\ R_3MHgOOMR_3 + (R_3M)_2Hg \rightarrow 2R_3MHgOMR_3\ ;\\ R_3MHgOMR_3 \rightarrow Hg + R_3MOMR_3\ ;\\ M{=}Si,\ \text{or}\ Ge;\ R{=}Et,\ \text{or}\ Ph.\ \end{gathered} \qquad (9)$$

When R = Et, the dimetalloxanes produced are responsible for the autocatalytic oxidation of the OMC. However, in the autoxidation of $(Ph_3Ge)_2Hg$, hexaphenyldigermanoxane is catalytically inactive[80].

The interaction of $(Et_3Ge)_2Hg$ and $(Et_3Si)_2Hg$ (0°C, alkanes) with oxygen is accelerated by small amounts of added ligands (NH_3, amines, pyridine, Ph_3P, etc.)[74–77]. The nature of the process and the kinetic parameters correspond to a catalytic reaction with formation of an

OMC–ligand complex [Eqn. (8)]. The peroxide formed is involved in competing catalytic decomposition reactions with the ligand L [Eqn. (10)] and reactions with the initial OMC [Eqn. (9)]:

$$\mathrm{Et_3}M\mathrm{HgOO}M\mathrm{Et_3} \xrightarrow{L} \mathrm{Et_3}M\mathrm{OO}M\mathrm{Et_3} + \mathrm{Hg}\ . \qquad (10)$$

There is also a possibility of the catalytic decomposition of the hydroxy-derivative formed under these conditions[79]:

$$\mathrm{Et_3MHgOMEt_3} \xrightarrow{L} \mathrm{Et_3}M\mathrm{OMEt_3} + \mathrm{Hg}\ .$$

Under certain conditions (high ligand concentration), the reaction proceeds wholly in accordance with the Eqn. (10).[76]

In the oxidation of $(Et_3Ge)_3Sb$ in n-octane at 18°C in accordance with the equation

$$2\,(\mathrm{Et_3Ge})_3\,\mathrm{Sb} + 3\mathrm{O_2} \rightarrow 3\,(\mathrm{Et_3Ge})_2\,\mathrm{O} + \mathrm{Sb_2O_3}\ ,$$

the autoxidation mechanism varies as a function of association of the initial compound from a reaction without the formation of free radicals (for polyassociated species) to a free-radical chain process [for the monomeric form $(Et_3Ge)_3Sb$].[81,82]

$[(i\text{-}Pr)_3Ge]_2Hg$ oxidises via a free-radical mechanism, which distinguishes this compound from the ethyl analogue. The comparatively high oxidation temperature (approximately 50°C) creates conditions for the thermal homolysis of the peroxy- and hydroxy-derivatives formed in the initial stage[83,84]:

$$\mathrm{i\text{-}Pr_3Ge\,HgOOGe\,(Pr\text{-}i)_3} \rightarrow \mathrm{i\text{-}Pr_3GeHg^{\bullet}} + \mathrm{i\text{-}Pr_3GeOO^{\bullet}}\ ;$$
$$\mathrm{i\text{-}Pr_3GeHgOGe\,(Pr\text{-}i)_3} \rightarrow \mathrm{i\text{-}Pr_3GeHg^{\bullet}} + {}^{\bullet}\mathrm{OGe\,(Pr\text{-}i)_3}\ .$$

The addition of an inhibitor reduces sharply the rate of oxidation of the initial OMC.

The formation of triethylsilyl peroxide in the autoxidation of ethyl(triethylsilyl)mercury is explained by radical reactions[85]:

$$2\mathrm{Et_3SiHgEt} \rightarrow \mathrm{Et_2Hg} + \mathrm{Et_3SiHg^{\bullet}} + \mathrm{Et_3}Si^{\bullet}\ ;$$
$$\mathrm{Et_3Si^{\bullet}} + \mathrm{O_2} \rightarrow \mathrm{Et_3}Si\mathrm{O_2^{\bullet}}\ ;$$
$$\mathrm{Et_3SiO_2^{\bullet}} + \mathrm{Et_3SiHgEt} - \left[\begin{array}{l} \rightarrow \mathrm{Et_3}Si\mathrm{OHgEt} + \mathrm{Et_3}Si\mathrm{O^{\bullet}} \\ \rightarrow \mathrm{Et_3}Si\mathrm{OOSiEt_3} + \mathrm{EtHg^{\bullet}}\ . \end{array}\right.$$

A wide variety of products, due to different intermediate and side reactions, are frequently formed in the autoxidation of OMC; particular mention should be made of the processes caused by the reactions of peroxides with OMC. Evidently the knowledge of the nature of these reactions is important for a general understanding of the mechanism of the formation and chemical reactions of OMPC. It is therefore useful to consider in greater detail the reactions of OMC with organic peroxides and the peroxides of organo-element derivatives.

Depending on the nature of the initial compounds and the reaction conditions, the nature of the interaction of OMC with peroxides may vary markedly, the reaction can proceed with or without the formation of OMPC. The mechanism of these processes can be both heterolytic and homolytic and is frequently very complex. An interesting heterolytic reaction of OMC with organic peroxides and peroxides of organo-element derivatives is nucleophilic substitution. It takes place with retention of the O–O bond and is therefore the basis of the principal method for the synthesis of OMPC. The reaction proceeds in accordance with the general equation

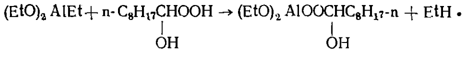
$$\mathrm{R}_{n-1}\mathrm{MX} + \mathrm{R'OOY} \rightarrow R_{n-1}\mathrm{MOOR'} + \mathrm{XY}\ , \qquad (11)$$

where $n \geqslant 1$, M = metal, R = alkyl or aryl, R′ = metal, hydrogen, or alkyl, X = OH, NH_2, NR_2, halogen, alkyl, aryl, alkoxy-group, aryloxy-group, or another substituent, and Y = metal or hydrogen. In many cases, reaction (11) is reversible and, in order to displace its equilibrium in the required direction, is carried out in the presence of bases (NH_3, amine, pyridine, etc.) or dehydrating agents (anhydrous sodium or magnesium sulphates).

A wide variety of OMPC have been obtained by reaction (11). For example, when organic peroxides were allowed to interact with lithium, sodium, and potassium halides, the pure peroxides of the alkali metals of the type ROOM [R = t-Bu, $(CH_3)_2PhC$, $(CH_3)Ph_2C$, or Ph_3C] were obtained in a crystalline state, which cannot be achieved in their synthesis by other methods[86–90].

Fully alkylated or arylated organocadmium and organomercury compounds react with hydroperoxides and the hydrocarbon group is substituted. The reactions are complicated both by the ready oxidation of the peroxide derived from the initial OMC, which failed to react, and by the peroxide decomposition reactions. In the case of organocadmium compounds, there is a possibility of the formation of mono- and di-peroxy-derivatives, for example PhCdOOBu-t and $Cd(OOBu\text{-}t)_2$.[91] The mercury compounds R_2Hg (R = n- and i-Pr or Ph) react with t-BuOOH to form the monoperoxy-compound only, which cannot be isolated owing to its further reactions under the conditions of the synthesis (at 70–100°C) in accordance with Eqns. (5) and (7).[92–96] Analogous reactions of the intermediate peroxy-compound occur when $RHgCCl_3$ (R = n- and i-Pr or Ph) reacts with t-BuOOH (80°C).[46] Fairly stable organomercury peroxides were obtained from the sodium salt of cumenyl hydroperoxide and ethyl- or phenyl-mercury chloride[97,98] or the derivatives of the latter XC_6H_4HgCl (X = *p*-Cl or *p*-CH_3O) in toluene solution[99]. The less stable compound $PhCH_2HgOOC(CH_3)_2Ph$[96] and the mercury diperoxide $[Ph(CH_3)_2COO]_2Hg$ were obtained similarly[100].

Fully alkylated or arylated derivatives of aluminium and thallium also readily undergo the substitution of the organic group for the peroxy-group. In the reaction of Ph_3Al with t-butyl or cumenyl hydroperoxides (at room temperature in toluene), the peroxide Ph_2AlOOR was not isolated, since it is readily converted into the aryloxy-derivative[101]. In the reaction of $(EtO)_3Al$ with $Ph(CH_3)_2.COOH$ or of the diethoxy-derivative $(EtO)_2AlCl$ with the salt of this hydroperoxide, the peroxide $(EtO)_2AlOOC.(CH_3)_2Ph$ was isolated and characterised[54,102]. When alkoxy- and alkyl groups are attached to an aluminium atom simultaneously, the alkyl group is substituted by the peroxy-group in the reaction with ROOH:



$$\mathrm{(EtO)_2\,AlEt} + \mathrm{n\text{-}C_8H_{17}\underset{\displaystyle\mathrm{OH}}{\underset{|}{\mathrm{C}}}HOOH} \rightarrow \mathrm{(EtO)_2\,AlOO\underset{\displaystyle\mathrm{OH}}{\underset{|}{\mathrm{C}}}HC_8H_{17}\text{-}n} + \mathrm{EtH}\ .$$

Under the reaction conditions, the peroxide formed is converted into the unstable polymeric peroxide $[-Al(O-)OOCH.(C_8H_{17}O-]n$.[103]

Fairly stable peroxides with a Tl–C bond have been obtained from organothallium compounds by nucleophilic substitution reactions. Depending on the reactant ratio, the reaction of Et_3Tl with pure H_2O_2 can give rise to both Et_2TlOOH (in 50% yield), which exists for several hours at 0–5°C, and the organothallium peroxide $Et_2TlOOTlEt_2$, which is stable at room temperature[104]. The peroxides Et_2TlOOR' [R′ = t-Bu or $Ph(CH_3)_2C$], which are stable under the usual conditions, are formed in high yields (60 to 80%) in the reaction of Et_3Tl with the corresponding hydroperoxides (at 0°C in benzene)[105]. The analogous reaction with triphenylgermyl hydroperoxide gave the organobimetallic peroxide $Et_2TlOOGePh_3$ (80% yield)[104,106]. The hydroperoxide Ph_3SiOOH reacts with Et_3Tl, but the peroxide formed under such conditions rearranges to $Et_2TlOSi(PhO)Ph_2$.[106]

Nucleophilic substitution reactions [Eqn. (11)] have been used particularly successfully for the synthesis of peroxy-compounds of Group IVB elements having the structure R_3MOOR' and the organometallic peroxides $R_3M{-}OOM'R'_3$, both symmetric and asymmetric, with identical and different central metal atoms. Tertiary hydroperoxides and R_3SiX (X = Cl, Br, or NEt_2) gave, in the presence of bases at temperatures between 0° and −5°C, the stable organosilicon peroxides $R_3SiOOCR'R''R'''$ ($R = CH_3$, Et, or Ph and R′, R″, and R‴ = CH_3 or Ph),[107-111] while secondary hydroperoxides gave $R_3MOOCH(CH_3)Ph$ (M = Si, Ge, or Sn; $R = CH_3$, Et, or n-Pr).[112] Hydrogen peroxide and chlorosilanes react in the presence of ammonia to form symmetrical organosilicon peroxides with identical and different groups attached to the silicon atom, namely $R_3SiOOSiR_3$ ($R = CH_3$, Et, n-Pr, or Ph)[113,114] and $R_2R'SiOOSiR'R_2$ ($R = CH_3$ or Ph; $R' = CH_3Ph$, *p*-BrC_6H_4, or *p*-$CH_3OC_6H_4$).[115-117] The asymmetric organosilicon peroxides $Ph_3SiOOSiR_3$ ($R = CH_3$, Et, n-Pr, n-Bu, n-C_5H_{11}, n-C_6H_{13}, or Ph),[110,118,119] and $Ph_3SiOOSi(CH_3)_2R$ (R = n-Bu, Ph, *p*-BrC_6H_4, *p*-$CH_3C_6H_4$, or *p*-$CH_3OC_6H_4$),[115,120] and the organo-dimetallic peroxides $R'R''R'''SiOOGePh_3$ (R′, R″, R‴ = CH_3, Ph, Et, n-Pr, n-Bu, or n-C_5H_{11})[118,121,122] have been synthesised by reaction (11) from hydroperoxides of organic derivatives of the elements and alkyl(aryl)silicon halides.

A series of stable dialkyl(aryl)-t-alkylperoxychlorosilanes have been obtained recently by a novel procedure[123]. They are synthesised by the reaction of $RR'SiCl_2$ with t-alkylperoxymagnesium chlorides in molar proportions of 1 : 1:

$$RR'SiCl_2 + R''OOMgCl \rightarrow RR'Si(OOR'')Cl + MgCl_2\ ;$$

$$R \text{ and } R' = CH_3,\ Et,\ CH{=}CH_2,\ CH_2Cl, \text{ or } Ph;$$

$$R'' = t\text{-}C_4H_9, \text{ or } t\text{-}C_5H_{11}.$$

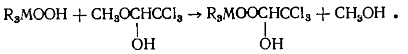
The substitution of the second chlorine atom takes place with difficulty even in the presence of a considerable excess of $R''OOMgCl$. Peroxides having the structure $RR'Si(OOR'')_2$ are obtained in small amounts under these conditions (approximately 6%). On the other hand, when chloroperoxysilanes are acted upon by alkyl hydroperoxides in the presence of ammonia or pyridine at 0°C, it is easy to obtain diperoxy-compounds derived from silicon and containing identical or different alkylperoxy-groups at the silicon atom[123]:

$$RR'Si(OOR'')Cl + R'''OOH \xrightarrow[(C_5H_5N)]{NH_3} RR'Si(OOR'')(OOR''') + HCl\ ;$$

$$R \text{ and } R' = CH_3,\ Et, \text{ or } Ph;\ R'' = t\text{-}C_4H_9;$$

$$R''' = t\text{-}C_4H_9,\ t\text{-}C_5H_{11}, \text{ or } C(CH_3)_2C_6H_{11}\ .$$

The reaction of the hydroperoxides Ph_3SiOOH and Ph_3GeOOH with the methyl hemiacetal of chloral (at room temperature in CH_2Cl_2 or $CHCl_3$ as solvent) is also interesting from the synthetic standpoint. The reaction gives fairly satisfactory yields of organosilicon and organogermanium peroxy-compounds containing functional groups in the alkylperoxy-group[124]:



$$R_3MOOH + CH_3O\underset{\displaystyle OH}{\underset{|}{C}}HCCl_3 \rightarrow R_3MOO\underset{\displaystyle OH}{\underset{|}{C}}HCCl_3 + CH_3OH\ .$$

When alkoxy or hydroxy-derivatives of alkyltin were used as the starting materials with the corresponding hydroperoxides, the organotin peroxides Et_3SnOOR' [R′ = t-Bu or $Ph(CH_3)_2C$] were obtained by reaction (11) and isolated in high yields (approximately 90%)[125]. The peroxide $Et_3SnOOBu$-s was obtained by the same method[126].

The nucleophilic substitution of an isocyanato-group linked to a Group IV element by an alkylperoxy-group has been demonstrated in the reaction of n-Bu_3MNCO and n-$Bu_2M(NCO)_2$ (M = Ge or Sn) with t-butyl and cumenyl hydroperoxides. The reaction proceeds readily at room temperature, but is complicated by the side reaction of the hydroperoxides with HNCO.[127]

The lead peroxides Et_3PbOOR' [R′ = t-Bu or $Ph(CH_3)_2C$], whose thermal stability is low, are formed from alkoxy-, hydroxy-, or oxo-derivatives of lead and hydroperoxides[128-130]. The solid peroxide $[Et_3PbOO(CH_3)_2C]_2C_6H_4$ was isolated in a fairly pure state after the reaction of Et_3PbOH with the dihydroperoxide derived from *p*-di-isopropylbenzene[128].

OMPC are not formed in the reactions with hydroperoxides of organolead and organotin compounds having M−M bonds. The metal−metal bond is dissociated, for example[131]:

$$(n\text{-}Bu_2Sn)_n + n\,t\text{-}BuOOH \rightarrow (n\text{-}Bu_2SnO)_n + n\,t\text{-}BuOH\ .$$

In the analogous reaction with cumenyl hydroperoxide (at 15−20°C in n-hexane or n-nonane), hexaethyldilead is readily converted into $Et_3PbOC(CH_3)_2Ph$ and Et_3PbOH, which undergo the substitution of their functional groups by the peroxy-group in the presence of an excess of the hydroperoxide[128].

Phenylderivatives of phosphorus(V) and antimony(V) undergo the substitution of one Ph group for the alkylperoxy-group in reactions with hydroperoxides. Pentaphenylantimony (Ph_5Sb) reacts with t-BuOOH and $Ph(CH_3)_2.COOH$ at room temperature in absolute pyridine giving a quantitative yield of the stable peroxides Ph_4SbOOR',[132] which can also be obtained in high yields from the hydroperoxide salts $R'OOM$ [M = Na or Li; R′ = t-Bu, Ph $Ph(CH_3)_2C$, $Ph_2(CH_3)C$, or Ph_3C] and tetraphenylstibonium halides[133]. The reaction of Ph_5P with t-BuOOH in pyridine, dioxan, or ether proceeds in a more complex manner, but its main pathway (80−85%) also involves the formation of an intermediate peroxide which immediately decomposes[132]:

$$Ph_5P + t\text{-}BuOOH \xrightarrow{-PhH} [Ph_4POOBu\text{-}t] \rightarrow Ph_3PO + PhOH + (CH_3)_2C{=}CH_2\ .$$

In the reactions of Ph_5P or benzyloxytetraphenylphosphorus with Ph_3SiOOH and Ph_3GeOOH, peroxy-compounds were not isolated either, because they isomerised to non-peroxy-products at the instant of formation[134]:

$$Ph_4PR + Ph_3MOOH \xrightarrow{-RH} [Ph_4POOMPh_3] \rightarrow Ph_3P(OPh)OMPh_3\ ;$$

$$R{=}Ph, \text{ or } OCH_2Ph;\ M{=}Si, \text{ or } Ge.$$

The same hydroperoxides and Ph_3SnOOH react with Ph_4SbBr in the presence of triethylamine to form the organobimetallic peroxides $Ph_4SbOOMPh_3$ (M = Si, Ge, or Sn), which were isolated in a pure form[135]. The mixed diperoxide of antimony and silicon $Ph_3Sb(OOSiPh_3)_2$ can be obtained by treating a mixture of t-butyl hydroperoxide and Ph_3SiOOH with Ph_3Sb:[136]

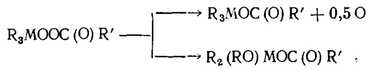
$$Ph_3Sb + t\text{-}BuOOH + 2Ph_3SiOOH \xrightarrow{-H_2O} Ph_3Sb(OOSiPh_3)_2 + t\text{-}BuOH\ .$$

The attempts to synthesise compounds of the peroxyester type by the nucleophilic substitution of alkyl or functional groups in OMC by acyl hydroperoxides were unsuccessful. The peracyl compounds obtained via the reaction

$$R_{n-1}MX + R'CO_3H \rightarrow R_{n-1}MOOC(O)R' + HX$$

(M = Hg, Sn, or Ph; R and R′ = alkyl or aryl, and X = OH, OR″, or $OCOCH_3$; M = Tl, R = Et, R′ = alkyl, and X = Et or OH).

either decompose immediately with liberation of oxygen (organomercury and organothallium derivatives)[104,137-139] or rearrange (organotin and organolead derivatives)[140-143]. Depending on the nature of the group R, for the latter compounds these two pathways can compete[143-146]:



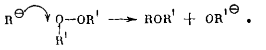
$$R_3MOOC(O)R' \rightarrow R_3MOC(O)R' + 0{,}5\,O_2 \quad ; \quad R_3MOOC(O)R' \rightarrow R_2(RO)MOC(O)R'$$

and, for the diperacyl derivative of diphenyltin, they are equally probable[147]. The intermediate diperoxides formed in the reaction of $Et_2Pb(OH)_2$ and $Et_2Sn(OH)_2$ with percapric acid decompose quantitatively to oxygen and the diethylmetal dicaprate[147,148]. Thus the reactions of OMC with peroxides containing an acid hydrogen atom (with hydroperoxides and peracids) lead to the formation of more or less stable OMPC. The reactions of OMC with other peroxy-compounds—alkyl and acyl peroxides and peroxyesters—are more varied. These reactions are not usually accompanied by the formation of OMPC. Depending on the nature of the peroxy-compound and the metal in the OMC, they can proceed either heterolytically or with intermediate formation of reactive OMC–peroxide complexes, which subsequently undergo both heterolytic and homolytic reactions. Such a mechanism is characteristic of the reactions of peroxides with electron-deficient compounds (those of Groups II and III). Many reactions of OMC with peroxides proceed as free-radical chain processes. In the first stage, the peroxide decomposes to free radicals, which then react with the OMC. The reactions of the above peroxides with OMC of Group IV elements takes place in this way. The peroxides can also act as oxidants, for example, in reactions with organic compounds of metals with free electron pairs [phosphorus(III) and antimony(III)]. The reactions of OMC with peroxy-compounds have been examined fairly completely in our previous reviews[2,149] and here we shall therefore merely give a brief survey of the results of studies by the Gorky group of chemists.

The reactions of organolithium compounds with alkyl peroxides involve the heterolysis of the peroxy-group and depend significantly on the nature of the organic group in the OMC and the peroxide. Alkyl-lithium compounds interact with alkyl peroxides to form asymmetric ethers and lithium alkoxides in accordance with the equation

$$RLi + R'OOR' \rightarrow R'OLi + ROR' \quad . \qquad (12)$$

Kinetic studies on the reactions of RLi (R = Et or n-Bu) with t-butyl and cumenyl peroxides[150,151] confirm the earlier hypothesis[152] that the OMC of Group I metals react with alkylperoxides via an S_N2 mechanism:



$$R^{\ominus} + \underset{R'}{O}{-}OR' \longrightarrow ROR' + OR'^{\ominus} \quad . \qquad (13)$$

However the interpretation of the mechanism of reaction (12) from the standpoint of one-electron transfer and the formation of a radical pair, reacting both within and outside the solvent cage[153], is also supported by some evidence, for example:

$$EtLi + t\text{-}BuOOBu\text{-}t \rightarrow [Et^{\bullet},\ t\text{-}BuO^{\bullet}] + t\text{-}BuOLi \ .$$

In view of the foregoing, the results obtained in the study of the reactions of compounds of the type R_3MLi with organic peroxides and peroxides of organic derivatives of the elements are of interest[154]. In the series of organobimetallic compounds having an M–M bond, the compounds R_3MLi exhibit the greatest polarity of this bond and behave at the same time as weaker nucleophiles than RLi. The reactions of R_3MLi [M = Ge or Sn; R = Et or $(CH_3)_3SiCH_2$] with t-butyl peroxide, benzoyl peroxide, dicyclohexyl percarbonate, and peroxides of organic derivatives of the elements and organometallic compounds proceed under mild conditions and involve nucleophilic attack by the R_3M anion on one of the peroxide oxygen atoms. In asymmetric peroxides of organic derivatives of the elements, the nature of the nucleophilic cleavage of bonds depends on the nature of the nucleophile, the steric effects of the substituents at the peroxy-group, and other factors.

The reactions of R_3MLi with t-butyl peroxide in tetrahydrofuran (THF) proceed in accordance with Eqn.(13) and the products are t-BuOLi and R_3MOBu-t [M = Sn or Ge; R = Et or $(CH_3)_3SiCH_2$]. When M = Ge and R = Et, the yield of Et_3GeOBu-t is low (11%), since the alkoxy-derivative enters in its turn into a nucleophilic substitution reaction with the initial OMC:

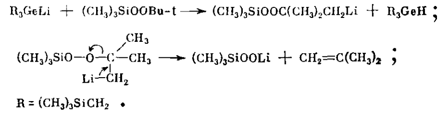
$$Et_3GeOBu\text{-}t + Et_3GeLi \rightarrow Et_3Ge{-}GeEt_3 + t\text{-}BuOLi \ . \qquad (14)$$

The compounds R_3MLi ($R_3M = Et_3Ge$), $[(CH_3)_3SiCH_2]_3Ge$, and $[(CH_3)_3SiCH_2]_3Sn$ are involved in reactions (13) and (14) with bis(trimethylsilyl) peroxide, which is known to be more reactive in relation to nucleophiles than t-butyl peroxide.

In the reaction of $[(CH_3)_3SiCH_2]_3SnLi$ with t-butylperoxytrimethylsilane and t-butylperoxytriphenylgermane, the R_3Sn anion attacks the oxygen atom linked to the t-butyl group in the peroxide[154,156]:

$$R_3SnLi + R'_3MOOBu\text{-}t \xrightarrow{THF} R_3SnOBu\text{-}t + R'_3MOLi$$
$$R = (CH_3)_3SiCH_2;\ R'_3M = (CH_3)_3Si,\ \text{or}\ Ph_3Ge.$$

On the other hand, in the reaction of the germyl analogue R_3GeLi with a silyl peroxide, products, the formation of which is probably due to the metallation of the t-butyl group of the peroxide in the initial stage followed by the elimination of isobutene, were obtained in high yields. The oxygen–oxygen bond does not dissociate under these conditions[154]:

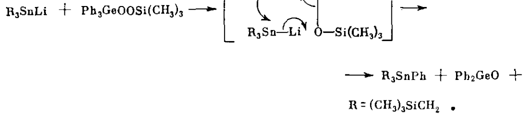


$$R_3GeLi + (CH_3)_3SiOOBu\text{-}t \longrightarrow (CH_3)_3SiOOC(CH_3)_2CH_2Li + R_3GeH \ ;$$
$$(CH_3)_3SiO{-}O{-}\underset{Li{-}CH_2}{\overset{CH_3}{C}}{-}CH_3 \longrightarrow (CH_3)_3SiOOLi + CH_2{=}C(CH_3)_2 \ ;$$
$$R = (CH_3)_3SiCH_2 \ .$$

The reactions of R_3GeLi with $Ph_3GeOOBu$-t and $Ph_3GeOOSi(CH_3)_3$ proceed in accordance with Eqn.(13), the R_3Ge anion attacking the oxygen atom linked to the Ph_3Ge fragment of the peroxide, for example:

$$R_3GeLi + Ph_3GeOOSi(CH_3)_3 \rightarrow R_3GeOGePh_3 + (CH_3)_3SiOLi \ ; \qquad (15)$$
$$R = (CH_3)_3SiCH_2 \ .$$

The reaction of the tin analogue with the latter peroxide leads to the formation of the phenylation product:



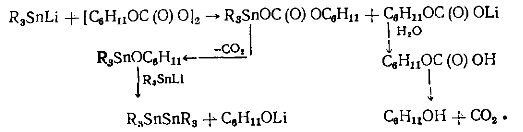
$$R_3SnLi + Ph_3GeOOSi(CH_3)_3 \longrightarrow \left[\begin{matrix} Ph{-}GePh_2{-}O \\ R_3Sn{-}Li \quad O{-}Si(CH_3)_3 \end{matrix}\right] \longrightarrow R_3SnPh + Ph_2GeO + (CH_3)_3SiOLi \ ;$$
$$R = (CH_3)_3SiCH_2 \ .$$

The reaction with the symmetric peroxide $Ph_3GeOOGePh_3$ does not involve phenylation and proceeds in accordance with mechanism (15).

Acyl peroxides (benzoyl peroxide and dicyclohexyl percarbonate) and t-butyl perbenzoate interact with R_3SnLi, the process likewise involving the heterolysis of the peroxy linkage[154]:

$$R_3SnLi + PhC(O)OOR' \xrightarrow{-R'OLi} R_3SnOC(O)Ph \xrightarrow{R_3SnLi} R_3SnSnR_3 + PhC(O)OLi \ ;$$

$$R{=}(CH_3)_3SiCH_2;\ R'{=}PhC(O),\ t\text{-}Bu\ .$$

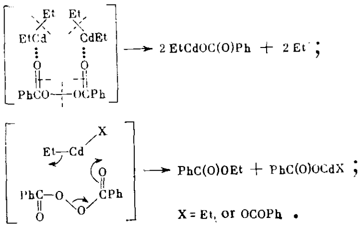


$$\begin{tikzcd}[column sep=small] R_3SnLi + [C_6H_{11}OC(O)O]_2 \arrow[r] & R_3SnOC(O)OC_6H_{11} \arrow[dl, "-CO_2"'] & + & C_6H_{11}OC(O)OLi \arrow[d, "H_2O"] \\ R_3SnOC_6H_{11} \arrow[d, "R_3SnLi"] & & & C_6H_{11}OC(O)OH \arrow[d] \\ R_3SnSnR_3 + C_6H_{11}OLi & & & C_6H_{11}OH + CO_2\ . \end{tikzcd}$$

In the similar reactions of R_2Mg (R = Ph or n-C_5H_{11}) with alkyl peroxides, only one Mg–C bond undergoes heterolytic cleavage[61,157–159]:

$$R_2Mg + R'OOR' \rightarrow RMgOR' + ROR'\ .$$

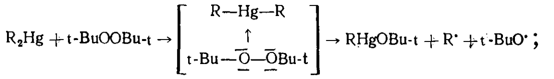
A characteristic feature of the reactions of organocadmium and organomercury compounds R_2M (M = Cd and R = Et or Ph; M = Hg and R = Ph) with benzoyl peroxide is the formation of 1 : 1 and 2 : 1 donor–acceptor complexes, in which there is a possibility of both heterolytic and homolytic cleavage of bonds[91,160]. The reactions involving the 1 : 1 complex take place without the formation of free radicals, while the M–C and O–O bonds undergo homolytic dissociation in the decomposition of the 2 : 1 complex. For example, in the case of cadmium we have



$Ph_3SiOCdR$ (R = CH_3 or Et) react similarly with benzoyl peroxide in benzene. The Cd–C and O–O bonds are dissociated in the coordination complexes formed, while the Si–O–Cd linkage persists[43].

The reactions of the dialkylmercury compounds R_2Hg with benzoyl peroxide lead to the formation of a more complex mixture of products. Free-radical processes also play a significant role in the reaction[96,160,161]. Thus, in the reaction of i-Pr_2Hg, benzoic acid, propane, propene, CO_2, and mercury were isolated in addition to isopropylmercury benzoate.

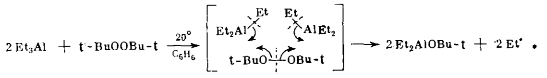
Organomercury compounds react with alkyl peroxides also via OMC–peroxide complexes, which decompose with formation of radicals, initiating the subsequent decomposition of the initial OMC in the reactions of the latter with the solvent[92–94,162]:



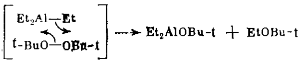
$$R_2Hg + t\text{-}BuOOBu\text{-}t \rightarrow \left[\begin{matrix} R{-}Hg{-}R \\ \uparrow \\ t\text{-}Bu{-}\bar{\underline{O}}{-}\bar{\underline{O}}Bu\text{-}t \end{matrix}\right] \rightarrow RHgOBu\text{-}t + R^{\cdot} + t\text{-}BuO^{\cdot}\ ;$$

$$R{=}n\text{- or } i\text{-}Pr.$$

The reactivity of organic derivatives of Group III elements in relation to alkyl and acyl peroxides is in many respects determined by the nature of the metal. Thus Et_3Al reacts with t-butyl peroxide similarly to organocadmium compounds[163,164]:

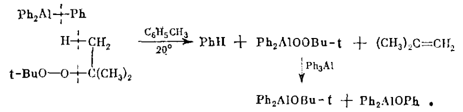


The formation of ether is due to a side reaction involving a heterolytic transformation of the 1 : 1 complex:



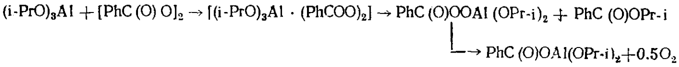
The etherate of triethylaluminium and the complex $Et_3Al.Ph_3P$ do not interact with t-butyl peroxide at room temperature[165]. The low reactivity of the Al–C bond in etherates persists also in the compound $(Ph_3Si)_2AlEt$ with the Si–Al bond[166].

In contrast to alkyl derivatives, Ph_3Al reacts with t-butyl peroxide with the intermediate formation of an organoaluminium peroxide, which then reacts with the initial OMC:[101,163]



Organoaluminium compounds react with acyl peroxides more vigorously than with alkyl peroxides. The reaction of benzoyl peroxide with Et_3Al in solution proceeds even below 0°C.[164,167,168] As for t-butyl peroxide, the reactions proceed with the intermediate formation of donor–acceptor complexes having OMC : peroxide ratios of 2 : 1 and 1 : 1 and decomposing homolytically and heterolytically respectively.

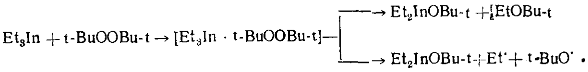
When the alkyl group in an organoaluminium compound is substituted by an alkoxy-group, the probability of heterolytic processes is enhanced. Such behaviour has been noted, for example, in the reaction of dicyclohexyl peroxydicarbonate with $Et_2AlOC_6H_{11}$ and Et_2AlOBu-n and also in the reactions of benzoyl and acetylbenzoyl peroxides with $EtAl(OEt)_2$.[169] However, the reactions of Et_2AlOCH_3 and Et_2AlOBu-s with benzoyl peroxide involve mainly the formation of a 2 : 1 complex, which decomposes homolytically[170]. On the other hand, when aluminium tri-isopropoxide reacts with benzoyl peroxide, the intermediate peroxy-compound is formed[171,172]:



$$\begin{tikzcd}[column sep=small] (i\text{-}PrO)_3Al + [PhC(O)O]_2 \arrow[r] & {[(i\text{-}PrO)_3Al\cdot(PhCOO)_2]} \arrow[r] & PhC(O)OOAl(OPr\text{-}i)_2 \arrow[d] + PhC(O)OPr\text{-}i \\ & & PhC(O)OAl(OPr\text{-}i)_2 + 0.5O_2. \end{tikzcd} \qquad (16)$$

In the reactions of acyl peroxides with the etherate of Et_3Al or the complex $Et_3Al.Ph_3P$ at room temperature, the donor is displaced in the first stage and intermediate 2 : 1 and 1 : 1 complexes are then formed. The ratio of the products of the homolytic and heterolytic decomposition of these complexes depends on the nature of the ligand. Thus $Et_3Al.Ph_3P$ reacts with benzoyl peroxide mainly homolytically, while in the reaction of the etherate the two pathways compete[165]. The complex $(Ph_3Si)_2AlEt.2LiBr.2THF$ reacts with benzoyl peroxide in the same way as with t-butyl peroxide, the process involving the preferential cleavage of the Si–Al bond[166].

Triethylindium and triethylthallium have a reduced electron-accepting capacity. Their reaction with t-butyl peroxide therefore proceeds with much greater difficulty than the reaction of Et_3Al. The reaction of Et_3In with the peroxide begins only at 50°C and Et_3Tl reacts at a still higher temperature (100°C).[173] A complex, which can subsequently decompose heterolytically and homolytically, is also formed in the first stage, for example:



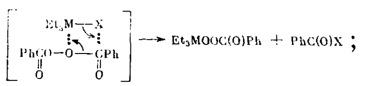
$$Et_3In + t\text{-}BuOOBu\text{-}t \rightarrow [Et_3In\cdot t\text{-}BuOOBu\text{-}t] \begin{cases} \rightarrow Et_2InOBu\text{-}t + EtOBu\text{-}t \\ \rightarrow Et_2InOBu\text{-}t + Et^{\cdot} + t\text{-}BuO^{\cdot}\ . \end{cases}$$

The mechanism of the reaction of Et_3Tl with acyl peroxides is analogous to that of the reaction of Et_3Al.[167,174,175]

When one ethyl group in Et_3Tl is substituted by an isopropoxy-group, the reaction with benzoy peroxide (at approximately 20°C) involves the heterolytic cleavage of the Tl–O bond in the organothallium compound and the C–O bond in the peroxide. As in reaction (16), the perbenzoate formed decomposes with liberation of oxygen[176]. The reaction of benzoyl peroxide with a siloxy-derivative of diethylthallium (at 40–50°C) involves the heterolytic dissociation of the Si–O bond in the OMC–peroxide complex with formation of a peracyl derivative of silicon, which rearranges[176]:

$$\begin{array}{l} \mathrm{Et_2TlOSiPh_3 + (PhCOO)_2 \rightarrow Ph_3SiOOC\,(O)\,Ph + Et_2TlOCOPh} \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{Ph_2\,(PhO)\,SiOC\,(O)\,Ph}\ . \end{array} \tag{17}$$

There is a wide variety of reactions of organic compounds of Group IV elements with alkyl and acyl peroxides. The nature of the reactions is determined both by the nature of the heteroatom and by the structure of the organometallic and peroxy-compounds. There is a possibility of reactions involving the intermediate formation of a reactive complex and, as in the alkoxy-derivatives of aluminium and thallium discussed above, in this complex the heterolytic transformations can occur with retention of the O–O bond and the formation of OMPC:[108,177,178]



$M{=}Sn$; $X{=}OCH_3$, OEt, OC_6H_{11}-cyclo,

OPh, or OCH_2Ph .

$M{=}Si$; $X{=}NEt_2$.

Peresters of organic derivatives of the elements undergo a heterolytic rearrangement (M = Sn or Si) via mechanism (17) and decompose to a slight extent with liberation of oxygen (M = Si). There is also a possibility of the dissociation of the O–O bond in the reaction complex, for example in the reaction of Et_3SnNEt_2 with benzoyl peroxide[108].

The hydrides of Group IV elements having organic substituents (R_3MH) do not react with benzoyl or t-butyl peroxide at room temperature. Their interaction is observed only at the temperature corresponding to the decomposition of the peroxide into radicals. For example, benzoyl peroxide reacts with Et_3SiH in the presence of oxygen and a solvent at 95–97°C. The main reaction products are triethylsilyl benzoate, benzoic acid, and carbon dioxide[179]. Benzoyloxy-radicals decompose or abstract hydride hydrogen from the OMC, forming triethylsilyl radicals $Et_3Si^{\cdot}$:

$$\mathrm{Et_3SiH + PhC\,(O)\,O^{\cdot} \rightarrow PhC\,(O)\,OH + Et_3Si^{\cdot}}\ ;$$

$$\mathrm{Et_3Si^{\cdot} + PhC\,(O)\,OOC\,(O)\,Ph \rightarrow Et_3SiOC\,(O)\,Ph + PhC\,(O)\,O^{\cdot}}\ .$$

The formation of free organosilyl radicals $R_3Si^{\cdot}$ (R = alkyl or aryl) in reactions of silicon hydrides with t-butyl peroxide has been noted[180,181]. Using ESR, it has recently been possible to demonstrate the formation of triorganogermyl radicals R_3Ge in the reaction of R_3GeH (R = alkyl or phenyl) with t-$BuO^{\cdot}$ radicals obtained on photolysis of t-butyl peroxide[182]. The radical mechanism of the reactions of organotin hydrides with alkyl and acyl peroxides has been confirmed by the use of labelled peroxides. It has been established that the reaction involving diacyl peroxide has a chain mechanism and that stannyl radicals ($R_3Sn^{\cdot}$) initiate the decomposition of the peroxide. The reaction of organotin hydrides with t-butyl or t-butylcumenyl peroxide has a radical but non-chain mechanism and organometallic radicals do not initiate the decomposition of the peroxide even at a fairly high temperature (130°C).[183,184]

Tetra-alkyl compounds R_4M (M = Si, Ge, Sn, or Pb) also react with t-butyl, benzoyl, or acetylbenzoyl peroxides and with peresters only at the temperature corresponding to the decomposition of the peroxy-compounds into free radicals[179,185–190]. In these reactions, Et_4Si and Et_4Ge behave as hydrogen donors:

$$\mathrm{Et_4M + R^{\cdot} \rightarrow RH + Et_3M\dot{C}_2H_4}\ ;$$

$M{=}Si$, Ge, Sn; $R{=}CH_3$, Ph, t-BuO, RC(O)O·.

The radicals derived from the peroxides behave in the same way in the reaction with hexaethyldisilane. The Si–Si bond is not dissociated under these conditions[191]:

$$\mathrm{R^{\cdot} + Et_3Si{-}SiEt_3 \rightarrow RH + Et_3Si{-}SiEt_2\dot{C}_2H_4}\ .$$

Secondary organosilicon radicals recombine, while $Et_3Ge\dot{C}_2H_4$ radicals undergo slight decomposition at the M–C bond in addition to dimerisation[185]:

$$\mathrm{Et_3M\dot{C}_2H_4 \rightarrow C_2H_4 + Et_3M^{\cdot}}\ ;$$

$M{=}Ge$, Sn.

The radical $Et_3Sn\dot{C}_2H_4$ does not dimerise and merely decomposes in accordance with the last equation[185,188–190].

The radicals derived from the peroxide do not behave merely as hydrogen acceptors and are capable also of displacing ethyl radicals from the molecule. Only this reaction proceeds with Et_4Pb:[189,190]

$$\begin{array}{c} \mathrm{Et_4M + R^{\cdot} \rightarrow Et_3MR + Et^{\cdot}}\ ; \\ \mathrm{M{=}Sn,\ Pb;\ R{=}t\text{-}BuO,\ PhC\,(O)O}\ . \end{array} \tag{18}$$

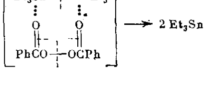
Ethyl radicals disproportionate or react with the initial OMC.

The replacement of the ethyl group in Et_4Sn by a halogen or the benzoyloxy-group does not alter significantly the nature of the interaction with benzoyl peroxide. The formation of all the products detected can be readily accounted for by the free-radical reaction (18). However, this is accompanied by a cryptoradical transformation in the cyclic complex[178,179]. Similar results have been obtained in the reactions of peroxides with tetrapropyl- and tetraisopropyl-tin and in the reaction of t-butyl peroxide with Et_6Sn_2.[189,191]

The reactions of phenyl derivatives of Group IV elements have been hardly investigated. In one of the first studies on these lines[192], it was established that Ph_4Pb does not react with acetyl peroxide, which decomposes and interacts with the solvent. However, in the reaction of $(CH_3)_3SnPh$ with benzoyl peroxide, the bond between the metal and the benzene ring undergoes homolytic cleavage[190]:

$$\mathrm{PhC\,(O)\,O^{\cdot} + (CH_3)_3\,SnPh \rightarrow (CH_3)_3SnOC\,(O)\,Ph + Ph^{\cdot}}\ .$$

The reactions of acyl peroxides with organic derivatives of Group IV metals having metal–metal bonds differ markedly from the reactions of R_4M. Thus the interaction of Et_6Sn_2 with benzoyl and acetylbenzoyl peroxides and dicyclohexyl percarbonate proceeds under very mild conditions and is not characterised by the wide variety of products usually observed in free-radical processes. According to some workers[189,193–197], the reaction proceeds via a stage involving the formation of an unstable cyclic complex, for example:



in which the Sn–Sn and O–O bonds dissociate homolytically without the formation of free-radicals. The absence of any other parallel reactions was confirmed by the determination of the heat of reaction, which proved to be 108 kcal.[198] The cryptoradical mechanism has also been confirmed by the formation of the acetate derivative of the OMC in the reaction with acetylbenzoyl peroxide[195]. Et_6Pb_2 [128,195] and organotin compounds having chains of tin atoms[196,199–202] react similarly with benzoyl peroxide. Polymeric dibutyltin reacts exothermically with benzoyl peroxide, but under these conditions the Sn–Sn bond does not dissociate regardless of the reactant ratio, 1,2-dibenzoyloxy-1,1,2,2-tetrabutyldistannane being formed instead[131].

In the studies on the properties of organobimetallic compounds with M–M′–M groups (M is a Group IVB metal and M′ a metal belonging to another Group), reactions with organic peroxides are also widely investigated in order to be able to compare the behaviour of such compounds and OMC having an M–M bond.

The interaction of $(Et_3Ge)_2Cd$ with t-butyl hydroperoxide in hexane solution (at 0–5°C) proceeds with evolution of heat. The main reaction pathway is the oxidation of the OMC with a side process involving the selective alcoholysis of the OMC by the carbinol formed[203]:

$$(Et_3Ge)_2Cd + t\text{-}BuOOH \rightarrow Et_3GeCdOGeEt_3 + t\text{-}BuOH\ ,$$
$$(Et_3Ge)_2Cd + t\text{-}BuOH \rightarrow Et_3GeCdOBu\text{-}t + Et_3GeH\ .$$

Since $Et_3GeHgOGeEt_3$ is extremely unstable[79] even at temperatures below –20°C, free mercury $(Et_3Ge)_2O$, and t-BuOH were isolated in the analogous reaction of $(Et_3Ge)_2Hg$ with t-BuOOH. The reaction of t-butyl peroxide with $(Et_3Ge)_2Cd$ (at approximately 20°C) led to the isolation of a complex mixture of products, the formation of which can be explained by a mechanism involving one-electron transfer in the complex, where OMC behaves as the electron donor[203]:

$$(Et_3Ge)_2Cd + t\text{-}BuOOBu\text{-}t \rightarrow \begin{bmatrix} Et_3GeCd^{\oplus}\cdot GeEt_3 \\ t\text{-}BuO^{\ominus}\cdot OBu\text{-}t \end{bmatrix} \rightarrow Et_3GeCdOBu\text{-}t + t\text{-}BuO^{\cdot} + Et_3Ge^{\cdot}\ .$$

Triethylgermyl radicals dimerise and recombine with t-BuO˙ radicals. Apart from recombining, decomposing, and abstracting hydrogen, the latter induce the decomposition of the initial OMC:

$$(Et_3Ge)_2Cd + t\text{-}BuO^{\cdot} \rightarrow Et_3GeCdOBu\text{-}t + Et_3Ge^{\cdot}\ .$$

In contrast to the compound examined, its mercury analogue does not react even under the conditions of the photochemical decomposition of the peroxide[72].

Compounds of the type $[R_3M]_nM'$, where M is a Group IV element and M′ a Group II–VI element, react with acyl peroxides vigorously at room temperature, evolving heat, as in the case of Et_6Sn_2, and involving the intermediate formation of active cyclic complexes, decomposing via a cryptoradical mechanism[149,204,205].

The reactions are described by simple stoichiometric equations. When M′ = Cd, the corresponding metal benzoates are formed[206,207]:

$$(Et_3M_2)Cd + 2\,(PhCOO)_2 \rightarrow Cd\,(OCOPh)_2 + 2\,Et_3MOCOPh$$
$$M{=}Si \text{ or } Ge\ .$$

Compounds with Ge–Zn bonds react similarly[208]. In a study of the reaction of bis(triethylgermyl)cadmium with asymmetric peroxides, it was established that the formation of the activated transition complex is preceded by the orientation of the peroxide molecules relative to the polarised Ge–Cd bond[203]:

$$(Et_3Ge)_2Cd + PhC\,(O)\,OOR \rightarrow \begin{bmatrix} Et_3GeCd\text{—}GeEt_3 \\ \vdots\quad\ \vdots \\ PhC(O)\,O\text{—}O\text{—}R \end{bmatrix} \rightarrow Et_3GeCdOC\,(O)\,Ph + Et_3GeOR\ ;$$
$$R{=}CH_3C\,(O) \text{ or } t\text{-}Bu\ .$$

The mercury analogues $(Et_3M)_2Hg$ (M = Si or Ge) react in the same way with benzoyl peroxide and dicyclohexyl percarbonate[72,73,209,210]. The intermediate $Et_3MHgOC(O)R$ decomposes quantitatively under these conditions to metallic mercury and the corresponding derivative $Et_3MOC(O)R$:

$$(Et_3M)_2Hg + (RCOO)_2 \rightarrow Et_3MHgOC\,(O)\,R + Et_3MOC\,(O)\,R$$
$$Hg + Et_5MOC\,(O)\,R \longleftarrow$$
$$R{=}Ph \text{ or } OC_6H_{11}\text{-cyclo}\ .$$

In the analogous reaction of the thallium compound $(Et_3Ge)_3Tl$, the free metal is not liberated and, as for the cadmium compound, the products are the metal benzoates—thallium benzoate and triethylgermanium benzoate[211,212]. The metal M′ is liberated in a free state in the reactions of $(Et_3M)_nM'$ (where M = Si, Ge, or Sn and M′ = Sb, Bi,[213–215] or S, Se, Te [216]) with benzoyl peroxide, the products being the triethylmetal benzoates in accordance with the equations

$$2\,(Et_3M)_3M' + 3\,(PhCOO)_2 \rightarrow 2M' + 6Et_3MOC\,(O)\,Ph\ ;$$
$$M{=}Si,\ Ge \text{ or } Sn;\ M'{=}Sb \text{ or } Bi.$$
$$(Et_3M)_2M' + (PhCOO)_2 \rightarrow M' + 2\,Et_3MOC\,(O)Ph\ ;$$
$$M{=}Si,\ Ge \text{ or } Sn;\ M'{=}S,\ Se \text{ or } Te.$$

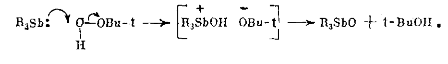
Acetyl peroxide reacts with $(Et_3Si)_2Te$, giving a quantitative yield of elemental tellurium and triethylsilicon benzoate and acetate[216].

The interaction of benzoyl peroxide with ethyl(triethylsilyl)mercury, having a single Si–Hg bond, is described by simple equations[72]:

$$2\,EtHgSiEt_3 + (PhCOO)_2 \rightarrow Et_2Hg + Hg + 2Et_3SiOCOPh\ .$$

This also applies to the reaction with compounds having several atoms of different metals linked to one another, for example $Et_3GeHgSiEt_3$ and $Et_3GeHgSiEt_2SiEt_3$,[73] and with compounds of the type R_3SiSeH.[217]

The reactions of alkyl derivatives of Group V elements with organic hydroperoxides are regarded as oxidation-reduction processes accompanied by the transition of the central element to the highest valence state and the reduction of the hydroperoxides to the corresponding alcohols. The reaction mechanism involves nucleophilic attack on peroxide oxygen by the OMC with the intermediate formation of an ion pair, for example:



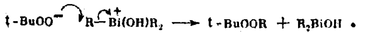
$$R_3Sb{:}\ \ \underset{\displaystyle H}{O}\text{—}OBu\text{-}t \longrightarrow \left[R_3\overset{+}{Sb}OH\ \ \overset{-}{O}Bu\text{-}t\right] \longrightarrow R_3SbO + t\text{-}BuOH\ .$$

The deprotonation of the 'onium cation in the ion pair leads to the formation of the oxide of the trialkyl derivative of the element (R_3SbO).[218]

In the reactions of trialkylbismuth R_3Bi (R = CH_3 or Et) with t-BuOOH, an ion pair is also formed in the initial stage. However, since the bismuth(V) state is less stable than the anitmony(V) state, the carbon atom attached to the bismuth atom and not hydrogen is subjected to nucleophilic attack in the bismuthonium ion $R_3\overset{+}{Bi}OH$. Ultimately the organobismuth compound is dealkylated without a change in the valence of bismuth. When $R_3\overset{+}{Bi}OH$ is attacked by the strongly nucleophilic peroxy-anion formed in the reversible reaction

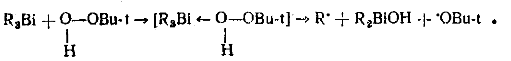
$$t\text{-BuO}^- + t\text{-BuOOH} \rightleftarrows t\text{-BuOH} + t\text{-BuOO}^- ,$$

an asymmetric dialkyl peroxide is produced:



$$t\text{-BuOO}^- \; R-\overset{+}{Bi}(OH)R_2 \longrightarrow t\text{-BuOOR} + R_2BiOH .$$

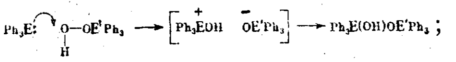
An ether and a carbinol are formed via similar reactions of alkoxide and hydroxide anions. It has also been established that the heterolytic process is accompanied to a slight extent by a homolytic reaction involving the homolysis of bonds induced by the molecules[218]:



$$R_3Bi + \underset{H}{O}-OBu\text{-}t \rightarrow [R_3Bi \leftarrow \underset{H}{O}-OBu\text{-}t] \rightarrow R^{\cdot} + R_2BiOH + {}^{\cdot}OBu\text{-}t .$$

Phenyl derivatives of phosphorus(III), arsenic(III), and antimony(III) are readily oxidised by t-butyl hydroperoxide to the corresponding oxides Ph_3EO, like the alkyl compounds. The rates of oxidation of Ph_3P and Ph_3Sb are approximately the same, while Ph_3As reacts with the hydroperoxide approximately sixty times more slowly. Such a change in rate has been explained by the presence of two opposed factors: the ability of *d* orbitals to form π bonds with the peroxy-group and the E–O bond energy[219].

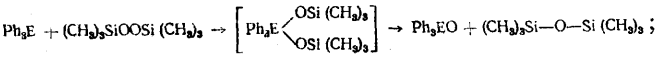
In similar reactions with the hydroperoxides Ph_3SiOOH and Ph_3GeOOH, the peroxide oxygen is subjected to nucleophilic attack by triphenylphosphine or triphenylantimony, but, in contrast to alkyl hydroperoxides, the 'onium cation is not deprotonated, a new element–oxygen–element bond being formed[136]:



$$Ph_3E{:} \; \underset{H}{O}-OE'Ph_3 \longrightarrow [Ph_3\overset{+}{E}OH \quad \overset{-}{O}E'Ph_3] \longrightarrow Ph_3E(OH)OE'Ph_3 ;$$

E = P or Sb; E' = Si or Ge.

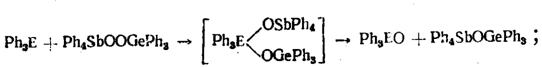
The symmetrical t-butyl peroxide is less reactive as an oxidant for Ph_3E. Whereas Ph_3P can be nevertheless converted into Ph_3PO at an elevated temperature (110° to 120°C) with formation of di-t-butyl ether, Ph_3As, Ph_3Sb, and Ph_3Bi do not react with t-butyl peroxide under these conditions[155]. Compared with the latter, bis(trimethylsilyl) peroxide is a more powerful oxidant. In the reaction with Ph_3P, Ph_3PO is formed quantitatively after a short time at a temperature as low as 25–60°C.[134,155,220] Ph_3As and Ph_3Sb react just as easily, but with a somewhat lower yield of the oxide product. However, triphenylbismuth is inert with respect to the action of this peroxide too[155]:



$$Ph_3E + (CH_3)_3SiOOSi(CH_3)_3 \rightarrow \left[Ph_3E\begin{matrix}OSi(CH_3)_3\\OSi(CH_3)_3\end{matrix}\right] \rightarrow Ph_3EO + (CH_3)_3Si-O-Si(CH_3)_3 ;$$

E = P or Sb .

The organometallic peroxide $Ph_4SbOOGePh_3$ reacts similarly with Ph_3P [134] and Ph_3Sb, forming two final products:



$$Ph_3E + Ph_4SbOOGePh_3 \rightarrow \left[Ph_3E\begin{matrix}OSbPh_4\\OGePh_3\end{matrix}\right] \rightarrow Ph_3EO + Ph_4SbOGePh_3 ;$$

E = P or Sb .

The foregoing data have shown that the reactions of OMC with oxygen and various peroxides proceed with formation of kinetically independent species having an unpaired electron. Because of this, the OMC–oxygen or OMC–peroxide systems can initiate various chain processes. The initiating capacity of such systems has been studied both in the polymerisation reactions of alkenes and their derivatives and in the reactions of OMC with various substrates. It is impossible to discuss this problem in detail in the present review. As an example, one may quote the initiation of the polymerisation of certain monomers by dialkylmercury or trialkylaluminium in the presence of oxygen[55,221–223] or by a trialkylboron–peroxide system[224] and the initiation of the oxidation of the solvent in the autoxidation of OMC, for example the oxidation of isopropyl alcohol or n-nonane in the reaction involving the oxidation of $i\text{-}Pr_2Hg$.[33,44,45,50] The initiation of the reactions of organomercury compounds of the type R_2Hg (R = alkyl or aryl) with polyhalogenomethanes by oxygen[47], perbenzoic acid[225], t-butyl hydroperoxide and peroxide[93,94], benzoyl peroxide[162,226], and peroxides obtained from cyclohexanone[227] has been noted. Acyl peroxides initiate the reactions of CCl_4 with tetraethylsilane[2,194,228], various organotin derivatives[192,194,195,229–231], and tetraphenyllead[192,230]. The conversion of mercury carboxylates into organomercury compounds, initiated by peroxides, is of interest from the preparative standpoint[232–234].

III. REACTIONS OF ORGANOMETALLIC PEROXY-COMPOUNDS

Organometallic peroxy-compounds are highly reactive. Their chemical reactions can occur in different ways, including both heterolytic and homolytic dissociation of the bonds in the molecule. In many cases, these reaction pathways operate simultaneously. For some peroxy-compounds, the reaction pathway can vary sharply as a function of conditions.

Heterolytic dissociation of the M–O bond in OMPC has been observed in their reactions with H_2O, HCl, and H_2SO_4. Peroxy-compounds of Group I–III elements are very readily hydrolysed by atmospheric moisture[59,88,90,98–100,104,106,235]. Hydroperoxides and organometallic peroxides give rise to the quantitative formation of H_2O_2 in this reaction, for example we have for thallium derivatives[104,106]:

$$\begin{gathered} Et_2TlOOH + H_2O \rightarrow Et_2TlOOH + H_2O_2 ; \\ Et_2TlOOTlEt_2 + 2H_2O \rightarrow 2Et_2TlOH + H_2O_2 . \end{gathered} \tag{19}$$

Alkylperoxy-derivatives gives rise to the corresponding hydroperoxides:

$$R_mMOOR' + H_2O \rightarrow R_mMOH + R'OOH , \tag{20}$$

where M is a Group I–III element. The reaction with hydrogen chloride or its alcoholic solution results in the formation of the corresponding alkyl(aryl) metal halides.

The sensitivity of the peroxides of Group IV elements to hydrolysis depends on the nature of the central metal atom and increases from silicon to lead. The compound Ph_3SiOOH is insensitive to hydrolysis under the usual conditions. In aqueous dioxan in the presence of sulphuric acid, the M–O bond is protolysed both in Ph_3SiOOH [236] and in Ph_3GeOOH and Ph_3SnOOH:[237]

$$Ph_3MOOH + H_2O \xrightarrow{H^+} Ph_3MOH + H_2O_2 ;$$

M=Si, Ge or Sn. .

The acid hydrogen atom in R_3MOOH may be substituted by a fragment comprising an organic derivative of the element in reactions with compounds such as Et_3Tl,[106] Ph_5P, and Ph_4POCH_2Ph,[134] and with Group IV and V metal halides[110,118–122,135,238]. The proton-donating capacity of hydroperoxides decreases in the sequence $Ph_3SiOOH > Ph_3GeOOH > Ph_3COOH > Ph_3SnOOH$ [239] and for triorganosilyl hydroperoxides the sequence is $Ph_3SiOOH > Ph_3COOH > (CH_3)_3.SiOOH$.[240]

Organosilicon peroxides of the type R_3SiOOR' and symmetrical and asymmetric peroxides of the type $R_3SiOOSiR'_3$ are fairly resistant to atmospheric moisture. The peroxide

$Et_3SiOOBu$-t is slowly hydrolysed by water to silanol and t-BuOOH,[107] while in the presence of acids the hydrolysis is faster.

The reaction of $Ph_3SiOOSbPh_4$ with HCl in benzene differs from the usual heterolysis of the Si–O bond[135]:

$$Ph_3SiOOSbPh_4 + HCl \rightarrow Ph_3SiOOH + Ph_4SbCl\ .$$

When this peroxide as well as its germyl and stannyl analogues interact with sulphuric acid, both M–O bonds are cleaved and H_2O_2 is formed[135].

All organotin and organolead peroxides are readily hydrolysable. When R_3MOOR' and R_3MOOMR_3 react with H_2O, acetic acid, or HCl, the Sn–O and Pb–O bonds are heterolysed and organic hydroperoxides or H_2O_2 are formed[23,71,128,129,237,241–244], as in reactions (19) and (20). There are isolated examples of the heterolysis of the O–O bond in certain organometallic compounds. Such cleavage of the O–O bond in organosilicon peroxides has been achieved under the influence of nucleophiles [RLi, EtONa, RMgX, and Ph_3E (E = P, As, or Sb)][155].

More typical reactions of OMPC involving the dissociation of the O–O bonds are the homolytic reactions occurring under the influence of heat, light, or radical initiation. The formation of radicals has been demonstrated in the thermal decomposition of the peroxy-compounds of the elements of all the Groups examined. In n-nonane, *m*-xylene, cumene, and t-butylbenzene solutions, Group I metal peroxides decompose at 80–130°C.[86–89,235,245,246] Thus $Ph(CH_3)_2COOLi$ decomposes to the extent of 80% in 3 h at 90°C [235] and the sodium derivative decomposes to the extent of 35% in 1 h at 80°C. The complex $Ph(CH_3)_2.COONa.Ph(CH_3)_2COOH$ is less stable, losing 80% of peroxide oxygen in 1 h at a temperature as low as 65°C.[89] The complex of potassium cumenyl peroxide with cumenyl hydroperoxide is also relatively unstable[245]. The thermal stability of alkali metal arylalkyl peroxides diminishes with increase of the number of phenyl groups. The peroxides decompose with homolysis of the O–O bond in the initial stage:

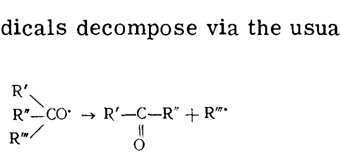
$$\begin{gathered} MOOR \rightarrow MO^{\cdot} + {}^{\cdot}OR\ ; \\ M{=}Li,\ Na\ \text{or}\ K;\quad R{=}t\text{-}Bu,\quad Ph\,(CH_3)_2C\ \text{or}\ Ph_2\,(CH_3)\,C,\ Ph_3C. \end{gathered} \tag{21}$$

The radicals formed dehydrogenate the solvent:

$$MO^{\cdot} + SH \rightarrow MOH + S^{\cdot}\ ; \tag{22}$$

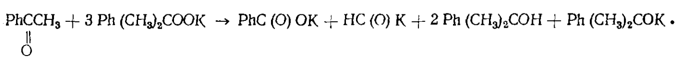
$$RO^{\cdot} + SH \rightarrow ROH + S^{\cdot}\ . \tag{23}$$

The tertiary $RO^{\cdot}$ radicals decompose via the usual mechanism:



$$R'R''R'''CO^{\cdot} \rightarrow R'{-}\underset{\underset{O}{\|}}{C}{-}R'' + R'''^{\cdot} \tag{24}$$

and can give rise to ketones, which in their turn enter into a molecular reaction with the initial OMPC. For example, potassium cumenyl peroxide decomposes to the extent of 60–80% via mechanism (21) and reacts to the extent of 20–40% in accordance with the equation



$$Ph\underset{\underset{O}{\|}}{C}CH_3 + 3\,Ph\,(CH_3)_2COOK \rightarrow PhC\,(O)\,OK + HC\,(O)\,K + 2\,Ph\,(CH_3)_2COH + Ph\,(CH_3)_2COK\ .$$

The thermal stability of mercury monoperoxides $RHgOOR'$ [R′ = t-Bu or $Ph(CH_3)_2C$] decreases in the series R = *p*-ClC_6H_4 > Ph > $PhCH_2$ > *p*-$CH_3OC_6H_4$ > Et > i-Pr.[98,247,248] t-Butylperoxy-derivatives of alkyl- and arylmercury are thermally less stable than the corresponding cumenylperoxy-derivatives. The peroxides decompose above 90°C with homolytic dissociation of the O–O bond and the formation of the oxy-radicals $R'O^{\cdot}$ and $RHgO^{\cdot}$, which, apart from their involvement in reactions (22) to (24), can also initiate the decomposition of the peroxide, for example, we have for $EtHgOOC(CH_3)_2Ph$:[97,248]

$$\begin{gathered} R'O^{\cdot} + EtHgOOC\,(CH_3)_2Ph \rightarrow R'OH + \\ + {}^{\cdot}C_2H_4HgOOC\,(CH_3)_2Ph \\ \longrightarrow C_2H_4 + HgO + Ph\,(CH_3)_2CO^{\cdot}\ ; \\ R' = Ph\,(CH_3)_2C\ \text{or}\ EtHg\ . \end{gathered}$$

Apart from dehydrogenating the solvent, the alkylmercuroxy-radicals decompose via the mechanism

$$EtHgO^{\cdot} \rightarrow Et^{\cdot} + HgO\ .$$

Alkyl radicals recombine and abstract hydrogen from the solvent. Dicumenylperoxymercury decomposes similarly (at 130°C in toluene)[100].

The radical decomposition of OMPC is frequently accompanied by a rearrangement of the peroxides, which can take place at the metal atom or at a tertiary carbon atom in the alkylperoxy-group. The isomeric transformation of the latter type with simultaneous homolytic decomposition has been observed in the photolysis of $EtHgOOC(CH_3)_2Ph$ (λ = 366 nm)[247]:

$$EtHgOOC\,(CH_3)_2Ph \xrightarrow{h\nu} EtHgOC\,(CH_3)_2OPh\ .$$

As already noted, organoaluminium peroxy-compounds, formed in the autoxidation of the alkyl derivatives R_3Al, are very readily converted into the isomeric alkoxy-derivatives when the molecule contains unoxidised groups. Such a possibility is ruled out in the absence of alkyl groups from the aluminium compound.

The compound $(EtO)_2AlOOC(CH_3)_2Ph$ is relatively stable at room temperature. After the hydrolysis of the decomposition products (at 90°C in xylene), $Ph(CH_3)_2COH$, $PhC(O)CH_3$, α-methylstyrene, ethyl alcohol, and aluminium hydroxide were found. It is suggested that these products are formed as a result of a radical reaction of the peroxide[102].

Thallium peroxides constitute an example of OMPC for which the influence of the peroxide structure on the nature of its reaction is a maximum. The decomposition of diethylthallium hydroperoxide is an example of the decomposition of a peroxide with evolution of oxygen. The hydroperoxide, which can be stored at 0–5°C for several hours, decomposes rapidly at room temperature[104]:

$$Et_2TlOOH \rightarrow Et_2TlOH + 0.5\,O_2\ .$$

Peracyl derivatives of thallium also decompose with evolution of oxygen and the formation of the corresponding diethylthallium carboxylates[137,139,249,250]:

$$\begin{gathered} Et_2TlOOC\,(O)\,R \rightarrow Et_2TlOC\,(O)\,R + 0.5O_2\ ; \\ R{=}CH_3,\ n\text{-}C_9H_{19}\ . \end{gathered}$$

The peroxides R_2TlOOR' [R = Et or Ph; R′ = t-Bu or $Ph(CH_3)_2C$] decompose in solution in n-nonane, toluene, cumene, and chlorobenzene at 100°C and above with dissociation of the O–O bond and the formation of radicals which are then involved in competing solvent decomposition and dehydrogenation reactions[105,249,250]:

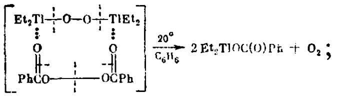
$$R_2TlOOR' \rightarrow R_2TlO^{\cdot} + {}^{\cdot}OR'\ . \tag{25}$$

The rate of decomposition increases with the initial concentration, which indicates the presence of an induced decomposition stage in the breakdown process. Apart from spontaneous homolysis via mechanism (25), autocatalytic decomposition of alkylperoxy-derivatives of diphenylthallium by one of the decomposition products (phenylthallium oxide) has been noted[249,250]. In contrast to tertiary alkylperoxy-derivatives of thallium, $Et_2TlOOEt$ undergoes molecular decomposition in solution in n-octane above 50°C:[59]

$$Et_2TlOOEt \rightarrow Et_2TlOH + CH_3CHO\ .$$

This results in the formation of diethylthallium hydroxide in a high yield (75–80%) and acetaldehyde (30%), which largely condenses under the influence of thallium hydroxide.

The organothallium peroxide $Et_2TlOOTlEt_2$ and the mixed peroxide of thallium and germanium, which are stable at room temperature, undergo an interesting reaction with benzoyl peroxide[104]:



$$Et_2TlOOGePh_3 + (PhCOO)_2 \longrightarrow Et_2TlOC(O)Ph + Ph_3GeOC(O)Ph + O_2\ .$$

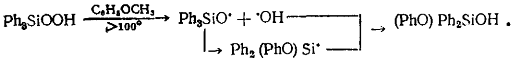
The study of the thermal transformation of the latter peroxide showed that it rearranges but only at the germanium atom and not at the thallium atom. It is interesting that, according to kinetic data, the reaction is bimolecular[106]:

$$Et_2TlOOGePh_3 \xrightarrow[80^\circ]{C_6H_5CH(CH_3)_2} Et_2TlOGe(OPh)Ph_2 \xrightarrow{H^+, H_2O} Et_2TlOH + Ph_2Ge(OH)OPh\ .$$

The silyl analogue rearranges similarly already during its preparation from Et_3Tl and Ph_3SiOOH.[106]

For the peroxy-compounds of Group IVB elements as well as thallium peroxides, there is a possibility of all types of reactions: spontaneous free-radical decompositions, including radical-induced stages, rearrangement at the central metal atom, and molecular decomposition, which is comparatively uncommon among OMPC.

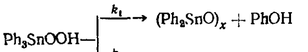
The thermolysis of Ph_3SiOOH is known[251] to proceed with the homolysis of the O–O bond in the initial stage:



$$Ph_3SiOOH \xrightarrow[>100^\circ]{C_6H_5OCH_3} Ph_3SiO^\cdot + {}^\cdot OH;\quad Ph_3SiO^\cdot \rightarrow Ph_2(PhO)Si^\cdot;\quad Ph_2(PhO)Si^\cdot + {}^\cdot OH \rightarrow (PhO)Ph_2SiOH\ . \qquad (26)$$

The formation of phenol among the products is explained by the rearrangement of the $Ph_3SiO^\cdot$ radical.

The decomposition of Ph_3SiOOH in chlorobenzene is catalysed by cobalt(II) salts (the stearate and abietate). The reaction proceeds under conditions where the thermal decomposition via mechanism (26) hardly occurs. The decomposition products are Ph_3SiOH, H_2O, and O_2 and there is no phenol[252]. Kinetic data for the influence of inhibitors and spectroscopic study of the valence transformations of the catalyst established that the decomposition under these conditions proceeds via a radical non-chain mechanism, similar to that of the catalytic decomposition of organic hydroperoxides. Cobalt stearate also catalyses the radical decomposition of Ph_3GeOOH, the rate of which is comparable to the rates of decomposition of the silicon analogue and Ph_3COOH.[253] In contrast to these hydroperoxides, the thermolysis of the least stable Ph_3SnOOH in benzene, toluene, dioxan, or acetonitrile at 10–40°C proceeds via two competing pathways:



$$Ph_3SnOOH \xrightarrow{k_1} (Ph_2SnO)_x + PhOH;\qquad Ph_3SnOOH \xrightarrow{k_2} Ph_3SnOH + 0.5\,O_2\ .$$

The ratio of the rates of decomposition varies little in different solvents and the reaction mixture does not catalyse the polymerisation of olefinic monomers[237].

Alkyl triorganosilyl peroxides R_3SiOOR' (R and R′ are alkyl groups) undergo homolytic decomposition on heating to a high temperature (170–200°C).[109,254–256] The dissociation energies of the O–O bond in a series of OMPC, including peroxy-compounds of silicon, have been determined by a thermochemical method[257]. The decomposition of $(CH_3)_3SiOOBu$-t in anisole, isopropylbenzene, n-nonane, and decane is described by the equation for first-order kinetics[254,256] and the rate of decomposition of the compounds $(CH_3)_3SiOOR'$, where R = $Ph(CH_3)_2C$, $Ph_2(CH_3)C$, or Ph_3C, increases steadily with increase of the number of phenyl groups[109,256]. The initial stage of the decomposition is homolysis of the O–O bond:

$$(CH_3)_3SiOOR' \rightarrow (CH_3)_3SiO^\cdot + {}^\cdot OR'\ . \qquad (27)$$

Tertiary alkoxy-radicals react via mechanisms (23) and (24). The radicals $Ph_3CO^\cdot$ and $Ph_2(CH_3)CO^\cdot$, formed via reaction (27) from the corresponding arylalkylperoxysilanes, are not only involved in these reactions but also undergo rearrangement:

$$2\,Ph_3CO^\cdot \rightarrow 2\,(PhO)Ph_2C^\cdot \rightarrow [(PhO)Ph_2C—]_2$$

In contrast to the tertiary alkoxy-radicals $RO^\cdot$, $(CH_3)_3SiO^\cdot$ radicals do not decompose and merely dehydrogenate the solvent:

$$(CH_3)_3SiO^\cdot + SH \rightarrow (CH_3)_3SiOH + S^\cdot\ . \qquad (28)$$

The decomposition of $Et_3SiOOBu$-t in hydrocarbons (nonane, decane) proceeds via a radical mechanism above 140°C, the decomposition products being C_2H_6, C_2H_4, t-BuOH, Et_3SiOH, Et_3SiOR, EtOH, and siloxane[107,258–260]. At 170° to 200°C, the process is complicated by the induced decomposition stage[258,259]. The decomposition of $Et_3GeOOBu$-t proceeds similarly[254].

The thermal stability of organosilicon peroxides R_3SiOOR' depends on the nature of the group R. In the series $(CH_3)_3SiOOCH(Ph)CH_3$, $Et_3SiOOCH(Ph)CH_3$, and n-$Pr_3SiOOCH(Ph)CH_3$, the thermal stability is a maximum for the first peroxide and a minimum for the last (in nonane at 180°C).[112] The thermal stability of the germyl analogues $(CH_3)_3GeOOCH(Ph)CH_3$ and $Et_3GeOOCH(Ph)CH_3$ is higher, the methyl derivative being the most stable[112]. According to kinetic data and the structure of the decomposition products, silyl peroxides incorporating a secondary alkylperoxy-group react simultaneously via three pathways. Apart from the homolytic decomposition in accordance with mechanism (27) and the subsequent reactions of the radicals via mechanisms (23), (24), and (28), the peroxide undergoes a rearrangement at the silicon atom with a synchronous redistribution of bonds in the active cyclic complex:

$$R_3SiOOCH(Ph)CH_3 \rightarrow (RO)R_2SiOCH(Ph)CH_3\ ; \qquad (29)$$

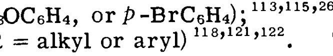
the peroxide also undergoes molecular decomposition to a ketone and silanol[261]:

$$R_3SiOOCH(Ph)CH_3 \rightarrow R_3SiOH + PhC(O)CH_3\ ;$$
$$R = CH_3,\ Et,\ n\text{-}Pr.$$

The possibility of the last pathway in the decomposition of the above peroxides has been confirmed by the formation of acetophenone.

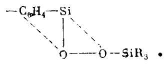
The thermal stability of the compounds $Ph_3SiOOCPh_n.(CH_3)_{3-n}$ as well as that of their ethyl analogues decreases as the phenyl groups accumulate in the peroxy-component[110,111]. The peroxide reacts via two simultaneous pathways in accordance with Eqns.(27) and (29); reaction (24) does not occur for $Ph_3SiOOCPh_3$.

The rearrangements of the OMPC of Group IV elements have been investigated in detail for symmetric and asymmetric organosilicon peroxides and mixed OMPC: $(R_3SiO-)_2$ (R = CH_3, Et, or n-C_6H_{13});[114] $[Ar_n(CH_3)_{3-n}.SiO-]_2$ (Ar = Ph, *p*-$CH_3OC_6H_4$, or *p*-BrC_6H_4);[113,115–117] $Ph_3SiOOSiR_3$ (R = CH_3, Et, n-Pr, n-Bu, n-C_5H_{11}, or n-C_6H_{13});[113,118,119,262,263] $Ph_3SiOOSi(CH_3)_2R$ (R = n-Bu, Ph, $CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, or *p*-BrC_6H_4);[113,115,262,264] $R_3SiOOGePh_3$ (R = alkyl or aryl)[118,121,122]. The thermal decomposition of these peroxides has been investigated in the temperature range 70–100°C and in different solvents. In inert solvents, the peroxides are converted into isomeric non-peroxy-compounds—aryl(alkyl)oxydisiloxanes:

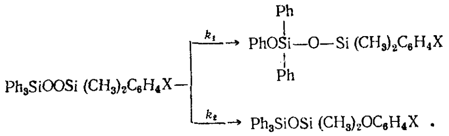


$$R{-}\overset{|}{\underset{|}{Si}}{-}O{-}O{-}\overset{|}{\underset{|}{Si}}{-} \rightarrow RO{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}\ .$$

The rearrangement is accompanied by the migration of the aryl or alkyl group from the silicon atom to the oxygen atom. The yield of rearrangement products is quantitative. The rate of rearrangement of the peroxides $[Ph_n(CH_3)_{3-n}SiO-]_2$ increases with increase of the number of phenyl groups. The results of kinetic measurements indicate a heterolytic mechanism of the rearrangement. One of the causes of the rearrangement is the effect of the $d\pi - p\pi$ conjugation between the silicon atom and the peroxide oxygen. The electron density deficit at the oxygen atoms increases following the introduction of electron-accepting groups into the moiety attached to silicon. It is noteworthy that the CH_3O and CH_3 groups in the *p*-position in the benzene ring of the peroxides $[p\text{-}XC_6H_4(CH_3)_2.SiO-]_2$ increase the rate constants for the rearrangement, the aryl group migrating, which is due to the more effective interaction of the π-electron cloud of the benzene ring with the *p* electrons of the oxygen atom in the cyclic transition complex:

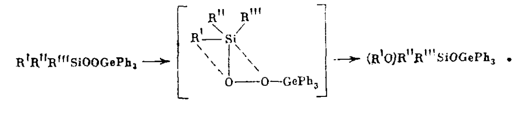


The rearrangement of the peroxides $p\text{-}XC_6H_4(CH_3)_2.SiOOSiPh_3$ is a complex reaction proceeding via two pathways[113,264]:



The relative capacities for migration of the aryl groups attached to different silicon atoms were determined by a kinetic method[113]. The rearrangement of the peroxides $Ph_3SiOOSiAlk_3$ proceeds exclusively via the migration of the Ph group from the silicon to the oxygen atom[113,119,262,263], the thermal stability decreasing with increase of the *I* effect of the alkyl groups in the sequence CH_3 > Et > n-Pr > n-Bu.[119]

On heating in the solid state or in solution above 100°C, the mixed organosilicon organogermanium peroxides $R_3SiOOGePh_3$ (R = CH_3, Et, n-Pr, n-Bu, n-C_5H_{11}, or Ph)[118,121,122] and $(CH_3)_2PhSiOOGePh_3$ [121] are quantitatively converted into a non-peroxy product. This involves the selective migration of the group attached to silicon:



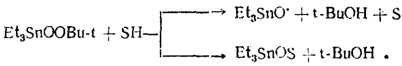
The rate of rearrangement increases with increase of solvent polarity and the number of phenyl groups attached to the silicon atom[118,121]. In terms of the rate of isomerisation, the compounds $Alk_3SiOOGePh_3$ can be arranged in the sequence CH_3 < Et < n-Pr < n-Bu < n-C_5H_{11} < Ph.[122] The factors which determine the pathway and rate of the rearrangement are as follows, as in the case of organosilicon peroxides: (1) electron density deficit at the peroxide linkage; (2) nucleophilic properties of the groups attached to silicon; (3) favourable energy of the cyclic transition state.

The relative basicities of peroxides of the type $R_3MOOM'R_3$ (M and M′ = Si or Ge; R = alkyl or aryl) and the relative migration capacities of the groups have been estimated spectroscopically[265,266] and the different pathways of the rearrangements undergone by these peroxides have been studied.

Peroxy-compounds of tin, such as the organotin peroxides R_3SnOOR' and the organostannyl peroxides $R_3SnOO.SnR_3$, are less stable than the corresponding silicon and germanium peroxides. The nature of the group R′ in the peroxide has an appreciable influence on the decomposition of Et_3SnOOR'. When R′ = Et, the peroxide decomposes comparatively rapidly in solution at room temperature[69,242,260]. The peroxides $(CH_3)_3SnOOBu$-t and $Et_3SnOOBu$-t are stable under the same conditions[254,259,260,267]. The main decomposition products of $Et_3SnOOBu$-t (in n-dodecane at 170°C) are $(Et_2SnO)_x$, $(Et_3Sn)_2O$, $Et_3SnOH.0.5H_2O$, t-BuOH, CH_3COCH_3, CH_4, C_2H_6, C_2H_4, and the dimerisation product of the dodecyl radical. The decomposition proceeds via radical and induced mechanisms: the initial stage involves the homolysis of the O–O bond:

$$Et_3SnOOBu\text{-}t \rightarrow Et_3SnO^{\cdot} + {}^{\cdot}OBu\text{-}t\ . \qquad (30)$$

This is followed by the competing decomposition reactions and the reactions of the radicals with the solvent and the peroxide. Apart from the radical process, the peroxide also undergoes a molecular transformation to $Et_2(EtO).SnOBu$-t similar to the rearrangement undergone by silyl peroxides and there is a competing molecular interaction of the initial peroxide with the solvent[268]:



The peroxide decomposition products at low initial concentrations indicate the absence of free $Et_3SnO^{\cdot}$ radicals. With increase of the concentration of the peroxide and temperature, the yield of products resulting from the radicals formed via mechanism (30) increases. The thermolysis of the peroxide is accelerated by the addition of $(Et_2SnO)_x$ and $(Et_3Sn)_2O$, which are involved in the radical reaction[269].

In connection with the possible formation of peroxides on oxidation of Et_4Sn and Et_6Sn_2, the influence of these compounds on the decomposition of organotin peroxides was studied. The addition of Et_4Sn to a solution of $Et_3SnOOBu$-t in n-decane (at 160°C) hardly alters the rate of decomposition of the peroxide, while the addition of Et_6Sn_2 greatly accelerates the decomposition. The reaction products are the same as in the decomposition of the peroxides in pure decane, but their proportions are altered[267]. In the presence of Et_6Sn_2, the compound Et_3SnOBu-t is formed in addition. The reaction has a radical chain mechanism with initial decomposition via mechanism (30). The radicals attack both the solvent and the OMC molecules, $Et_3SnO^{\cdot}$ radicals reacting preferentially with Et_4Sn, displacing $Et^{\cdot}$ radicals, rather than abstracting hydrogen:

$$Et_3SnO^{\cdot} + Et_4Sn \rightarrow Et_3SnOSnEt_3 + Et^{\cdot}\ .$$

In the decane$-\mathrm{Et_6Sn_2}$ system, the radical decomposition is accompanied by the molecular interaction of the peroxides with the OMC:

$$\mathrm{Et_3SnOOBu\text{-}t + Et_3SnSnEt_3 \rightarrow Et_3SnOSnEt_3 + Et_3SnOBu\text{-}t} \ .$$

The tin peroxide $\mathrm{Et_3SnOOBu}$-s, containing a secondary group, is less stable than the t-butylperoxy-derivative[126] and also less stable than its germanium and silicon analogues. In solution in n-dodecane, the decomposition is a first-order reaction with formation of $\mathrm{(Et_2SnO)_x}$, $\mathrm{(Et_3Sn)_2O}$, $\mathrm{CH_3C(O)Et}$, and $\mathrm{C_2H_6}$. A kinetic study showed that, in n-nonane, isopropylbenzene, and anisole (at 150° to 200°C), a rearrangement and molecular decomposition take place in addition to radical decomposition:

$$\mathrm{Et_3SnOOBu\text{-}s \rightarrow (EtO)\,Et_2SnOBu\text{-}s} \ ,$$
$$\mathrm{Et_3SnOOBu\text{-}s \rightarrow Et_3SnOH + CH_3C(O)Et} \ .$$

Molecular decomposition has also been suggested for the tin peroxide $\mathrm{Et_3SnOOCH_2Ph}$ with a primary alkylperoxy-group, formed in solution on photochemical oxidation of $\mathrm{Et_3SnCH_2Ph}$ by oxygen[67]:

$$\mathrm{Et_3SnOOCH_2Ph \rightarrow Et_3SnOH + PhCHO} \ .$$

Organotin peroxides with tertiary and secondary arylalkyl groups attached to peroxide oxygen, $\mathrm{Et_2SnOOC(CH_3)_2Ph}$ and $\mathrm{Et_3SnOOCH(CH_3)Ph}$, are less stable than the corresponding silicon and germanium derivatives[112,269]. The decomposition of the first peroxide (in octane at 140–170°C) is a first-order reaction. The products are determined by the reactions of the $\mathrm{Et_3SnO^{\cdot}}$ and arylalkoxy-radicals formed via mechanism (30). The peroxide also undergoes the decomposition induced by the solvent radicals[125,260,267,270], for example:

$$\mathrm{Et_3SnOOC(CH_3)_2Ph + S^{\cdot} \xrightarrow{-SH} CH_3\dot{C}HSnEt_2OOC(CH_3)_2Ph \rightarrow}$$
$$\mathrm{\rightarrow C_2H_4 + Et_2SnO + Ph(CH_3)_2CO^{\cdot}} \ .$$

The thermal stability of the phenyl derivative $\mathrm{Ph_3SnOOC.}$ $\mathrm{.(CH_3)_2Ph}$ is also lower than that of the germanium and silicon analogues. The peroxide decomposes at a measurable rate at a temperature as low as 130°C. Whereas homolytic decomposition of $\mathrm{Ph_3MOOC(CH_3)_2Ph}$ (where M = Si or Ge) at the O–O bond is accompanied by the simultaneous isomeric transformation into the phenoxy-derivative $\mathrm{(PhO)Ph_2MOC(CH_3)_2Ph}$, the organotin peroxide does not react under comparable conditions in anisole at 130°C. The radical mechanism includes the formation of $\mathrm{Ph(CH_3)_2CO^{\cdot}}$ and $\mathrm{Ph_3SnO^{\cdot}}$ radicals, the former giving rise to the induced decomposition of the peroxide:

$$\mathrm{Ph_3SnOOC(CH_3)_2Ph + Ph(CH_3)_2CO^{\cdot} \rightarrow Ph_3SnO^{\cdot} + Ph(CH_3)_2COOC(CH_3)Ph} \ ,$$

and the latter being capable of decomposition with ejection of the $\mathrm{Ph^{\cdot}}$ radical, instead of the $\mathrm{Ph_3SiO^{\cdot}}$ and $\mathrm{Ph_3GeO^{\cdot}}$ radicals[271]:

$$x\,\mathrm{Ph_3SnO^{\cdot} \rightarrow (Ph_2SnO)}_x + x\,\mathrm{Ph^{\cdot}} \ .$$

The organostannyl peroxides $\mathrm{R_3SnOOSnR_3}$ are thermally less stable than the peroxides of the type $\mathrm{R_2SnOOR'}$. For example, $\mathrm{Et_3SnOOSnEt_3}$ [61,63,241,243,244,272] decomposes at 0°C in the course of one day and explodes at 60°C. The decomposition in solution in n-nonane (at 20–80°C) proceeds with the quantitative formation of $\mathrm{Et_2SnO}$ and $\mathrm{EtOSnEt_3}$ as the final products. The reaction follows first-order kinetics and is induced by the radicals derived from the peroxide:

$$\mathrm{Et_3SnOOSnEt_3 \rightarrow 2\,Et_3SnO^{\cdot}} \ ;$$
$$\mathrm{Et_3SnOOSnEt_3 + Et_3SnO^{\cdot} \rightarrow Et_3SnOEt + Et_3SnOO\dot{S}nEt_2} \ ;$$
$$\begin{tikzcd}
 & \mathrm{Et_2SnO + Et_3SnO^{\cdot}} \\
\mathrm{Et_3SnOO\dot{S}nEt_2} \arrow[ur] \arrow[dr, "\mathrm{Et_3SnO^{\cdot}}"'] & \\
 & \mathrm{2\,Et_2SnO + Et_3SnOEt} \ .
\end{tikzcd}$$

The peroxide gives rise to the polymerisation of acrylonitrile and methyl methacrylate.

Among all the peroxides of Group IVB elements, the thermal stability of the organolead peroxides is lowest. Thus $\mathrm{Et_3PbOOBu}$-t and $\mathrm{Et_3PbOOC(CH_3)_2Ph}$ decompose slowly even at room temperature and rapidly with evolution of a gas on heating[69,128,129,243]. The decomposition has a radical mechanism and the reaction mixtures catalyse the polymerisation of olefins[69]. The autocatalytic decomposition of $\mathrm{Et_3PbOOBu}$-t has been noted (in hydrocarbons at 90–120°C), the rate of reaction increasing with increase of the initial concentration of the peroxide[254].

The peroxide $\mathrm{Ph_3PbOOC(CH_3)_2Ph}$ is the least stable of the compounds obtained in the $\mathrm{Ph_3MOOC(CH_3)_2Ph}$ series (M is a Group IV element)[271]. Very little benzene has been found in the autocatalytic decomposition products, since the $\mathrm{Ph_3PbO^{\cdot}}$ radicals do not decompose like the $\mathrm{Ph_3SnO^{\cdot}}$ radicals, giving rise to $\mathrm{Ph_3PbOH}$ as a result of the dehydrogenation of the solvent. The autocatalysis is due to the presence of diphenyl-lead oxide, formed as a result of the reactions of the hydroxide:

$$\mathrm{2\,Ph_3PbOH \rightarrow (Ph_3Pb)_2O + H_2O} \ ;$$
$$x\,\mathrm{(Ph_3Pb)_2O} \rightarrow x\,\mathrm{Ph_4Pb + (Ph_2PbO)}_x \ .$$

The addition of the oxide not only shortens the induction period, but also accelerates the decomposition of the peroxide owing to the formation of the less stable oxoperoxide[271]:

$$\mathrm{Ph_3PbOOC(CH_3)_2Ph + (Ph_2PbO)}_x \rightarrow \mathrm{Ph_3Pb(OPbPh_2)}_x\mathrm{OOC(CH_3)_2Ph} \ .$$

Radical and heterolytic reactions are characteristic of the peroxy-compounds of Group V elements, as for the peroxides of Group IV elements already mentioned. The homolytic decomposition of organoantimony peroxides $\mathrm{Ph_4SbOOR'}$ (R′ is a tertiary group) has been achieved under the influence of ultraviolet light[273], for example:

$$\mathrm{Ph_4SbOOBu\text{-}t \xrightarrow{h\nu} Ph_4SbO^{\cdot} + {}^{\cdot}OBu\text{-}t} \ ;$$
$$\mathrm{Ph_4SbO^{\cdot} \rightarrow Ph_3SbO + Ph^{\cdot}} \ .$$

In their interaction with the solvent (toluene and chlorobenzene) via a radical substitution mechanism, the $\mathrm{Ph^{\cdot}}$ and t-$\mathrm{BuO^{\cdot}}$ radicals give rise to benzene, a carbinol, and a mixture of isomeric methylbiphenyls or chlorobiphenyls. The decomposition of the peroxide induced by the solvent radicals has been noted in chlorobenzene as a side reaction. In chloroform, the stages involving the induced decomposition and photolysis of the peroxide at the O–O bond compete: in carbon tetrachloride, the induced decomposition is the main reaction pathway:

$$\mathrm{CCl_4 \xrightarrow{h\nu} Cl^{\cdot} + {}^{\cdot}CCl_3} \ ;$$
$$\mathrm{Ph_4SbOOR' + Cl^{\cdot} \rightarrow Ph_4SbCl + [{}^{\cdot}OOR']} \ .$$

The $\mathrm{{}^{\cdot}CCl_3}$ radicals frequently recombine and frequently interact with the peroxide:

$$\begin{tikzcd}
\mathrm{Ph_4SbOOR' + {}^{\cdot}CCl_3} \arrow[r] & \mathrm{Ph_4SbCCl_3 + [{}^{\cdot}OOR']} \arrow[dr] & \\
 & & \mathrm{Ph_4SbCl + :CCl_2} \ .
\end{tikzcd}$$

The addition of cyclohexene to $\mathrm{CHCl_3}$ or $\mathrm{CCl_4}$ lowers the contribution of the induced decomposition.

Under thermal decomposition conditions (in polar and non-polar solvents at 100°C), the peroxides $\mathrm{Ph_4SbOOR'}$ [R′ = t-Bu, $\mathrm{Ph(CH_3)_2C}$, $\mathrm{Ph_2(CH_3)C}$, or $\mathrm{Ph_3C}$] isomerise quantitatively to a non-peroxy product with migration of one phenyl group from the antimony atom to the oxygen atom[133]:

$$\mathrm{Ph_4SbOOR' \rightarrow Ph_3Sb(OPh)OR' \xrightarrow{2HCl} Ph_3SbCl_2 + PhOH + R'OH} \ .$$

The solvent is not involved in this reaction.

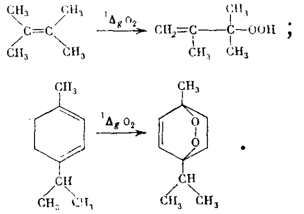
The mixed peroxides involving antimony and a Group IV element behave similarly on heating to 100°C in the solid state or in solution. The rearrangement again takes place at the antimony atom[135]:

$$Ph_4SbOOMPh_3 \xrightarrow{100^\circ} Ph_3Sb(OPh)OMPh_3 \rightarrow Ph_3SbO + Ph_3MOPh\ ;$$
$$M=Si,\ Ge\ \text{or}\ Sn.$$

Molecular decompositions are also possible for the peroxy-compounds of antimony. Bis(triphenylbromoantimony) peroxide $Ph_3(Br)SbOOSb(Br)Ph_3$ is fairly stable at room temperature in the crystalline state, but decomposes rapidly in solution. Two independent reactions then occur: molecular decomposition with elimination of oxygen and a rearrangement with simultaneous cleavage of the O–O bond and the migration of the Ph group from antimony to oxygen:

$$Ph_3(Br)SbOOSb(Br)Ph_3 \rightarrow Ph_3(Br)SbOSb(Br)Ph_3 + 0.5\ O_2\ ;$$
$$Ph_3(Br)SbOOSb(Br)Ph_3 \rightarrow Ph_2(PhO)(Br)SbOSb(Br)Ph_3\ .$$

The contribution of the decomposition of the peroxide via mechanism (31) is greater the higher the concentration of the peroxide in solution. It is of interest that the oxygen evolved is in an excited state and enters into reactions typical of singlet oxygen. In the decomposition of the peroxide in chlorobenzene with added tetramethylethylene or α-terpinene at 70°C, oxygen is hardly evolved, the product being 3-hydroperoxy-2,3-dimethylbut-1-ene or ascaridole respectively[274]:



The above brief review shows that OMPC constitute a very interesting class of compounds. However, in contrast to their formation and thermal decomposition reactions, the chemical reactions of the peroxides have been little investigated. One can state with confidence that new data will be obtained in the immediate future on the reactivities, structures, and the analysis of these compounds, and that practical applications will be suggested.

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Chemistry of Extraction by Sulphoxides

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The present state of the chemistry of extraction equilibria involving sulphoxides of diverse structure—aliphatic, cyclic, and also mixtures of petroleum origin—is discussed, and results are given for the extraction of inorganic and organic acids and metal salts from aqueous solution. Comparison of the extraction properties of neutral organophosphorus compounds with those of sulphoxides shows a promising future in liquid extraction for cyclic sulphoxides, especially those of petroleum origin. The mechanism of extraction is discussed, and the dependence of extraction properties on the molecular structure of the sulphoxide is considered. A list of 153 references is included.

CONTENTS

I. INTRODUCTION

Methods for the extraction of metals that have been successfully employed in chemical nuclear technology are now beginning to be widely introduced into the industry of rare and non-ferrous metals. The chemistry of extraction has been very intensively studied in connection with the spread of extraction methods for concentrating and separating elements. The variety of approaches and methods of investigation and the great scope of work on the chemistry of extraction equilibria have ensured the solution of many extraction problems. Methods have been found for extracting almost every element.

Nevertheless, the range of extractants used in industry for the extraction of metals has hitherto been narrow (mainly tributyl phosphate, di(2-ethylhexyl) hydrogen phosphate, and amines) and inadequate for technical processes in the hydrometallurgy of rare and non-ferrous metals. The cost of an extractant is an extremely important factor in its application in the technology of such metals. In this connection there is a very pressing need to find and investigate new and powerful extractants possessing high selectivity and chemical stability while being comparatively cheap and suitable for large-scale manufacture. Another acute problem is the search for extractants to remove various organic compounds such as carboxylic and sulphonic acids and also phenols from industrial solutions and sewage.

Among promising extractants must be included sulphoxides, both individual and those of petroleum origin[1]. Resources for production of the latter are almost unlimited. Tens of thousands of tons of sulphoxides a year can be obtained at negligible cost (400–600 roubles per tonne[2]) from a single fraction of diesel fuel from Arlansk petroleum of the Bashkir ASSR (or West Surgut petroleum of Western Siberia). This is possibly why interest in sulphoxides as extractants for metal salts and acids has grown considerably during recent years among both Soviet and foreign scientists. The number of studies on the extraction properties of sulphoxides increases from one year to the next. Work on the chemistry of complexes of sulphoxides with inorganic and organic compounds has even grown considerably more.

The aim of the present Review is to systematise published data and the Reviewers' own results on the extraction equilibria of sulphoxides with metal salts and acids. Consideration is given to the properties both of individual sulphoxides of diverse structure (aliphatic, aromatic, cyclic with different ring sizes, etc.), as well as sulphoxides of petroleum origin.

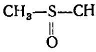
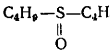
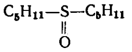
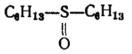
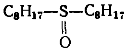
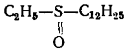
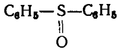
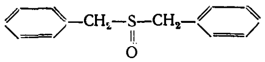
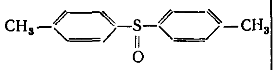
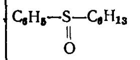
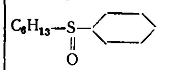
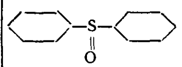
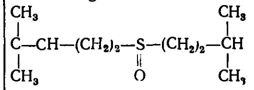
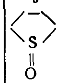
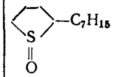
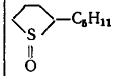
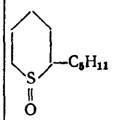
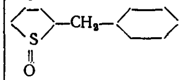
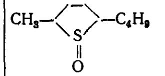
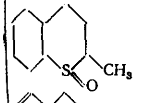
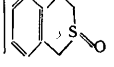
II. PLACE OF SULPHOXIDES AMONG EXTRACTANTS

Sulphoxides are organic oxides containing an S=O functional group. A quasi-tetrahedral configuration is probable for the molecule, in which one of the orbitals of the tetrahedron is represented by the lone pair of electrons of the sulphur atom. The molecular structure of sulphoxides agrees well with the chemical properties and with the assignment of the vibrational frequencies of the sulphinyl bond in the infrared and Raman spectra. Sulphur and oxygen atoms are joined not only by a σ bond but obviously also by interaction of a $3d$ orbital of sulphur with a $2p$ orbital of oxygen ($2p$–$3d$ hybridisation)[3,4]. Examination of the nature of the sulphur–oxygen bonds in a review[5] led to the conclusion that the electron cloud of an S=O double bond was displaced towards the oxygen atom. Recent studies also confirm a $\sigma + \pi$ bond[6,7].

Interaction of the sulphinyl group with the hydrocarbon substituents attached to the sulphur atom is inductive and electron-accepting in character, without involving conjugation, e.g. with aromatic and unsaturated radicals[8,9]. A carbon atom forming a bond with the sulphur atom is able to act as a donor of electrons (interaction of the lone pair of electrons of the sulphur with π orbitals of the hydrocarbon radical) and also as an acceptor of electrons (interaction of the d orbital of sulphur with π electrons of the hydrocarbon radical). The intramolecular interactions in the sulphoxide molecules and the character of the sulphur–oxygen bond govern the properties of these compounds towards complex formation and extraction. Sulphoxides for which data on these processes have been published are listed in Table 1.

Structure-group analysis of petroleum sulphides[10] indicates that petroleum sulphoxides are mixtures of

Table 1. Properties of most thoroughly studied sulphoxides in complex formation and extraction*.

Sulphoxide	Abbrevn.	Formula	M.p., °C	n_D^{20}	Sulphinyl sulphur, mass %	Ref.
Dimethyl	DMSO	 $CH_3-\underset{\underset{O}{\|}}{S}-CH_3$	—	1.4780	—	20, 22
Dibutyl	DBSO	 $C_4H_9-\underset{\underset{O}{\|}}{S}-C_4H_9$	35	—	—	49, 153
Dipentyl	DPSO	 $C_5H_{11}-\underset{\underset{O}{\|}}{S}-C_5H_{11}$	51	—	16.1	36
Dihexyl	DHSO	 $C_6H_{13}-\underset{\underset{O}{\|}}{S}-C_6H_{13}$	60	—	14.7	43, 51
Dioctyl	DOSO	 $C_8H_{17}-\underset{\underset{O}{\|}}{S}-C_8H_{17}$	71	—	—	33, 34
Dodecyl ethyl	DoESO	 $C_2H_5-\underset{\underset{O}{\|}}{S}-C_{12}H_{25}$	—	—	—	34
Diphenyl	DPhSO	 $C_6H_5-\underset{\underset{O}{\|}}{S}-C_6H_5$	70	—	15.8	51, 114
Dibenzyl	DBzSO		133	—	—	114
Di-*p*-tolyl	DpTSO		93	—	—	113
Hexyl phenyl	HPhSO	 $C_6H_5-\underset{\underset{O}{\|}}{S}-C_6H_{13}$	30	—	15.0	51
Cyclohexyl hexyl	ChHSO		48	—	14.7	51
Dicyclohexyl	DChSO		83	—	14.8	51
Di-isopentyl	DIPSO	 $\overset{CH_3}{\underset{CH_3}{C}}-CH-(CH_2)_2-\underset{\underset{O}{\|}}{S}-(CH_2)_2-\overset{CH_3}{\underset{CH_3}{CH}}$	40	—	16.3	134
Thiolan 1-oxide	TIO		—	1.5195	—	52, 153
2-Heptylthiolan 1-oxide	HTIO		—	1.4820	15.1	36
2-Pentylthiolan 1-oxide	PtIO		—	—	—	42
2-Pentylthian 1-oxide	PThO		—	1.4962	16.0	51
2-Cyclohexylmethylthiolan 1-oxide	ChMTIO		—	1.5204	15.3	36
2-Butyl-5-methylthiolan 1-oxide	BMTIO		—	1.4885	17.8	105
3-Methyl-2-thiabicyclo[4,4,0]decane 2-oxide	MTBDO		44	—	16.4	36
1,2,3,4-Tetrahydro-2-thianaphthalene 2-oxide	THThNO		77	—	18.2	36

*Different authors have published different melting points, molecular refractions, and other physicochemical constants for sulphoxides. More complete characterisation of the purity of the product would evidently require an indication of the concentration of sulphinyl sulphur determined by potentiometric titration[152].

mono-, bi-, and tri-cyclic thiolans mainly of saturated structure. In order to obtain petroleum sulphoxides sparingly soluble in water (and therefore suitable for extraction) use is made of concentrates of petroleum sulphides or directly distilled fractions of high-sulphur petroleums boiling over the range 260–360°C.[2] The petroleum sulphides are oxidised with hydrogen peroxide[11,12]. A concentrate of petroleum sulphides can be obtained in various ways[13], but preferably by extraction with sulphuric acid[14]. The molecular structure remains almost unchanged when petroleum sulphides are oxidised to sulphoxides, so that the structure-group analysis of the sulphoxides is similar to that of the petroleum sulphides.

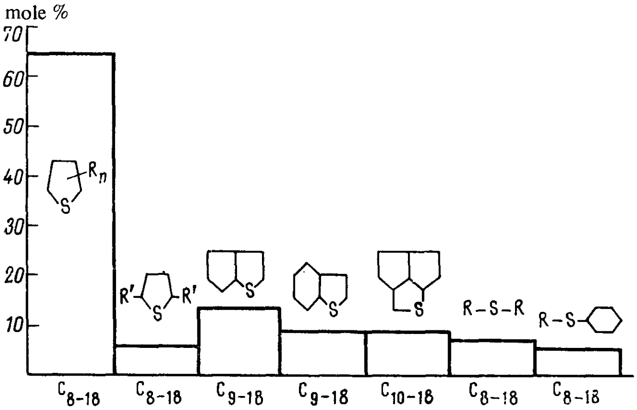


Figure 1. Relative contents of individual structural groups of sulphides and numbers of carbon atoms in molecules of concentrate of sulphides (190–360°C) from Arlansk petroleum.

Fig. 1 illustrates the composition of the most thoroughly studied sulphide concentrate of Arlansk petroleum (190–360°C).[10] Monocyclic and bicyclic thiolans evidently predominate. The composition of the petroleum sulphides is similar for the kerosene–gas-oil fractions of Western Surgutsk[15] and Romashkinsk[16] petroleums. The sulphides present in the kerosene–gas-oil fractions of petroleums confined to Devonian, Carboniferous, and Lower Cretaceous sandstones probably have similar structure-group analyses[17]. It follows from the structure-group composition of petroleum sulphides that the extraction properties of the sulphoxides can be compared with those of individual cyclic sulphides, which serve as model for the petroleum sulphoxides.

Metal salts and acids are usually dissociated and strongly hydrated in aqueous solution. In order to transfer them to an organic phase with a high partition coefficient on extraction it is therefore necessary to use a reagent having a strong tendency to complex formation, sufficient to overcome the bonds between the extractable compounds and water. Hence it is clear that the chemistry of extraction equilibria is closely related to that of complex formation.

The possible information by sulphoxides of complexes with metal salts and acids has been known for a long time. The study, carried out in 1907, of the interaction between iron(III) chloride and a sulphoxide led to isolation of an equimolecular complex[18]. The interaction of sulphoxides with gaseous hydrogen chloride was discovered in 1916.[19] Later the protonation of dimethyl sulphoxide in sulphuric acid was investigated and the basicity estimated[20], which was followed[21] by the preparation of complexes of sulphoxides with perchloric acid. Complex formation by sulphoxides in aqueous and alcoholic media was studied intensively on dimethyl sulphoxide at the beginning of the 1960s.[22–27] The first communications on the possibility of using sulphoxides as extractants date from this time.

Nikolaev et al. formulated general requirements which should be satisfied by extractants, and noted the need to study the class of extractants R_nElO, among which sulphoxides were mentioned[28,29]. The possibility of using sulphoxides as extractants was suggested also by Cotton and Francis[30] in a study of the ligand properties of dimethyl sulphoxide.

The first studies of the extraction properties of sulphoxides were made by Korpak[31–34], but he gave no quantitative interpretation of the extraction equilibria of sulphoxides with metal salts and acids. Nikolaev and his coworkers described the mechanism of extraction by sulphoxides[35–37]. Quantitative characteristics of extraction were obtained by the Reviewers[38–40], in the first investigation of the extractive properties of cyclic sulphoxides, which were found to model those of petroleum sulphoxides[41,42]. Papers giving quantitative characteristics of the mechanism of extraction by sulphoxides appeared also abroad[43–45].

Table 2. Basicity of extractants.

Extractant	p*K*	Ref.	Extractant	p*K*	Ref.
Diethyl ether	0.98	49	Di-isopentyl methylphosphonate	2.74	51
Oxolan	1.26	49	Trimethylphosphine oxide	3.49	49
Acetone	1.18	49	Dimethyl sulphoxide	2.53	49
Butan-2-one	1.18	49	Diphenyl sulphoxide	2.03	51
Cyclohexanone	1.30	49	Dihexyl sulphoxide	2.67	51
Triphenyl phosphate	1.73	49	Dicyclohexyl sulphoxide	2.77	51
Tributyl phosphate	2.56	51	2-Heptylthiolan 1-oxide	2.74	51

Before examining actual experimental results on the chemistry of extraction by sulphoxides, we shall discuss the position occupied by these compounds among oxygen-containing extractants (organic oxides) of type R_nXO. The latter form complexes with metal salts usually by an electronic mechanism of donor–acceptor interaction. The difference in extractive power (and in complex formation) among compounds R_nXO will be determined by the electron density on the oxygen atom†, as well as by the geometrical parameters of the molecules, which largely determine the entropy contribution.

Accurate determination (calculation) of electron density in polyatomic molecules R_nXO (where X = P, S, N, As, Se, etc.) is not yet possible at the present state of development of quantum chemistry, and the best comparative measure of the donor power of oxygen is the basicity of the extractant. This represents the free energy of protonation of the P=O, S=O, N=O, etc. groups[49]. Correlation of basicity with extractive power clearly establishes the position of sulphoxides in the sequence of organic oxides[50,51]. Table 2 indicates that they occur between ketones and phosphine oxides with respect to basicity; they occupy an intermediate position also with respect to extractive power. One reason for the enhanced reactivity of the sulphinyl in comparison with the carbonyl group is that the sulphur atom is larger than the carbon atom ($r_S = 1.04$ and $r_C = 0.77$ Å), and with a consequent diminished energy of bonding with oxygen ($E \propto e^{-m}$, where $m \geqslant 1$) and a smaller force constant k_e(SO).

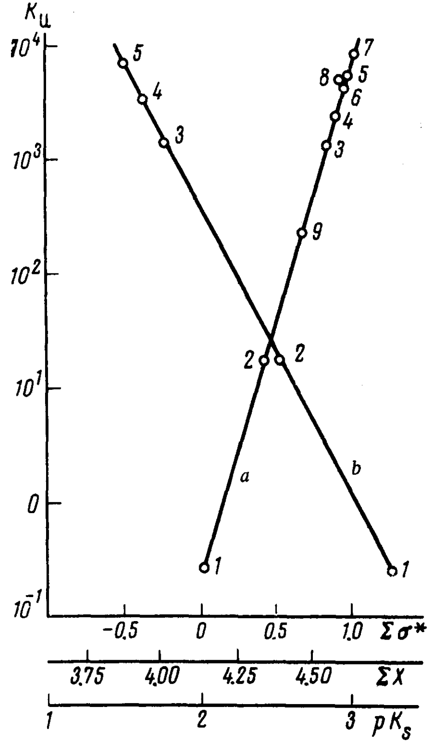


Figure 2. Dependence of extraction constants $\bar{K}_U$ for uranyl nitrate on: *A*) basicity pK_S; *B*) sum of electronegativities ΣX or Taft constants $\Sigma\sigma^*$ of: 1) DPhSO; 2) HPhSO; 3) DHSO; 4) [?]; 5) ChHSO; 6) HTlO; 7) PThO; 8) DPMP; 9) TBP.

The correlation between the basicity of sulphoxides and their extractive power for uranyl nitrate is well described by the equation[51]

$$\lg\bar{K}_U = -11.88 + 5.6\,pK_s \tag{1}$$

which is clearly confirmed by Fig. 2. On passing from dialkyl to cyclic sulphoxides both the basicity of the oxygen atom and the extractive power increase. Values of $\bar{K}_U$ for tributyl phosphate (TBP) and di-isopentyl methylphosphonate (DPMP) fit satisfactorily into the general

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† The coordination of metals to the sulphinyl oxygen atom has been established from the infrared spectra of the complexes isolated in numerous investigations. An exception is palladium, which is able to coordinate both with sulphur and with oxygen[46–48].

relationship. Dialkyl sulphoxides considerably surpass tributyl phosphate in extractive power, but are somewhat inferior to phosphonates, whereas cyclic sulphoxides are rather better than phosphonates. Cyclic sulphoxides are superior to aliphatic sulphoxides, of course, also in their complexing properties[52]. It must be concluded from the comparison of the extractive power of aliphatic sulphoxides that petroleum sulphoxides (PetrSO), being mixtures of cyclic sulphoxides, will surpass aliphatic sulphoxides and tributyl phosphate in extractive power. This view is supported by many experimental results[41,42,53,54].

The influence of structure is illustrated by Fig. 2, which shows good correlation of extractive power with basicity within a class of sulphoxides, but for open-chain sulphoxides the extractive power may be predicted, as for other neutral extractants[55], from the electronegativities ΣX or the inductive constants σ^* of substituents adjacent to the sulphur atom[51]:

$$\lg \bar{K}_U = 2.34 - 2.54 \sum \sigma^* = 3.04 - 5.23 \sum (X - 2). \quad (2)$$

Equations (1) and (2) give rise to a relation between the basicity of sulphoxides and the electronegativities of substituents:

$$pK_s = 2.54 - 0.47 \sum \sigma^* = 2.67 - 0.94 \sum (X - 2). \quad (3)$$

A similar relation is obtained from a consideration of the extractive power of sulphoxides for nitric acid[56]:

$$\lg \bar{K}_H = -0.64 - 0.92 \Sigma\sigma^*. \quad (4)$$

The extraction properties of sulphoxides are more sensitive than those of neutral organophosphorus compounds to change in the electronegativity of a substituent. Thus replacing one aliphatic group ($X = 2.0$) by phenyl ($X = 2.54$) in the latter type of compound diminishes the extraction of uranium by a factor of 17, but in sulphoxides by a factor of 40.

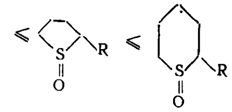
Table 3.

Compound	ν(SO), cm^{-1}	Compound	ν(PO), cm^{-1}
Dimethyl sulphoxide	1069	Tributyl phosphate	1274
Dibenzyl sulphoxide	1056	Triphenyl phosphate	1306
Benzyl phenyl sulphoxide	1054	Tributylphosphine oxide	1160
Diphenyl sulphoxide	1052	Triphenylphosphine oxide	1195

Another characteristic distinction is that extractive power cannot be predicted from the infrared spectra of sulphoxides, unlike those of neutral organophosphorus compounds. The introduction of aromatic substituents leaves the sulphur–oxygen stretching frequency almost unchanged[5,57–59], whereas the phosphorus–oxygen stretching frequency is raised[60] [Table 3]. Nor has the expected fall in absorption frequency ν(SO) been observed on passing to cyclic sulphoxides[59]. The improvement in extractive power on passing from aliphatic to cyclic sulphoxides is due not to an increase in energy of bonding of the resulting complexes but to the entropy factor[40].

From available data it may be concluded that on complex formation sulphoxides are more sensitive to molecular geometry than are neutral organophosphorus compounds. We note in conclusion that sulphoxides can be included in the sequence of neutral organic extractants of increasing extractive power:

$$R_2O < R_2CO < (RO)_3PO < R_2SO < (RO)_2R'PO \leqslant PetrSO \leqslant$$



$< R_3PO < R_3NO.$

III. EXTRACTION OF WATER AND INORGANIC ACIDS

Extraction of Water

Sulphoxides containing >10 carbon atoms are only sparingly soluble in water (0.1–4 g litre^{-1}),[44,61] but cyclic sulphoxides are rather more soluble. The use of salting-out agents during extraction lowers considerably the aqueous solubility of sulphoxides. Solubility is strongly influenced by the nature of the diluent. Thus it decreases by a factor of 200 in the sequence nonane–xylene–chloroform, and e.g. for petroleum sulphoxides in chloroform is 0.02 g litre^{-1}. The melting-point curves for aqueous dibutyl and di-isobutyl sulphoxides exhibit anomalies, but solid hydrates are not detected[62], which indicates weak interaction between the sulphoxides and water.

The extraction of water by sulphoxides can be represented by complex formation according to the equation

$$H_2O + qS \rightleftarrows H_2O \cdot qS, \quad (5)$$

where S is the sulphoxide and q the solvation number. When the activity of water is high ($a_{H_2O} > 0.6$) a monosolvate ($q = 1$) is formed[63]; with $a_{H_2O} > 0.4$ a disolvate appears[58,63]. The decrease in the solubility of water accompanying the decrease in its activity is slower than would be expected from the relation $[H_2O]_{org} \propto a_{H_2O}$. The influence of the diluent on the extraction of water by sulphoxides is analogous to that observed with tributyl phosphate[64]: the effective extraction constant of water K_{H_2O} diminishes in the sequence nonane–benzene–chloroform. The infrared spectra of sulphoxides with water exhibit no significant shift in the absorption frequency of the sulphinyl group, but a slight frequency shift in the symmetrical hydroxyl band (3640 cm^{-1}).[58] All this is evidence of comparatively weak interaction of the sulphoxide with water.

Extraction of Nitric Acid

The heightened interest in the extraction of nitric acid by sulphoxides[33,40] is due to the possible use of the latter as extractants of rare and radioactive elements from nitrate media. A sulphoxide will extract the acid by a solvation mechanism as an unhydrated monosolvate[65–72]:

$$H^+ + NO_3^{2-} + S \rightleftarrows HNO_3 \cdot S. \quad (6)$$

The extractive power for nitric acid diminishes with increase in size of the hydrocarbon group in the dialkyl sulphoxide[45]. That of cyclic sulphoxides[65] is greater than with dialkyl sulphoxides (K_H is ~1 and 0.78 respectively for 2-heptylthiolan 1-oxide and dipentyl sulphoxide, and the latter surpass tributyl phosphate and di-isopentyl methylphosphonate (0.2 and 0.33). The extraction of nitric acid is significantly influenced by the type of diluent of the sulphoxides. Thus K_H has the respective values 1.44 and 1.25 when alkanes[56] and aromatic hydrocarbons are used, whereas the values obtained with tetrachloromethane and chloroform are 0.70 and 0.26.[65] On extraction from concentrated nitric acid the acid concentration in the organic phase exceeds the stoichiometric value[69]. Direct calorimetric measurements of the interaction of nitric acid with various sulphoxides[73] show that the enthalpy of interaction of the second acid molecule with the monosolvate $HNO_3.S$ is considerably smaller than that of addition of the first acid molecule to the sulphoxide, and amounts to ~9 kcal mole^{-1}. The second molecule is probably attached to the anion of the acid in the monosolvate, as with tributyl phosphate. If the enthalpy of complex formation between nitric acid and sulphoxides depends on the groups attached to the sulphur atom, and for diheptyl, benzyl decyl, and diphenyl sulphoxides ΔH decreases from 30 to 28.7 and 24.8 kcal mole^{-1}.

The variation in entropy in this sequence does not exceed 0.8 e.u. The effective extraction constant of nitric acid by sulphoxides correlates with the enthalpy of extraction and is described by the equation[73]

$$\lg \bar{K}_H = -0.079 - 0.866\,\Delta H_{extr}\,. \tag{7}$$

Nevertheless, the extraction constant is almost independent of temperature[65], which indicates that entropy factors are decisive. The relatively large displacement of the sulphinyl absorption band in the infrared spectrum of the solvate of nitric acid to lower frequencies ($\Delta\nu$(SO) = 60 cm^{-1}) indicates a quite stable bond between the sulphinyl oxygen atom and the proton of the acid.

Hydrochloric Acid

In contrast to nitric acid, hydrochloric acid is extracted by a mechanism involving both hydration and solvation[74]:

$$H^+ + Cl^- + h\,H_2O + q\,S \rightleftarrows HCl \cdot h\,H_2O \cdot q\,S. \tag{8}$$

Solvation numbers q determined by various authors[33,63,75,76] vary from 1 to 3, which indicates the presence of mono-, di-, and tri-solvates in the organic phase. The hydration number h also varies, from 3 to 1: i.e. $q + h = 4$, in good agreement with the coordination number 4 generally accepted for the oxonium cation.

Extraction by sulphoxides becomes appreciable only when the concentration of the acid in the aqueous phase exceeds 4 M; the extraction constants are small[45]. When the concentration of the aqueous acid is 6–7 M, the extraction isotherm passes through a maximum (with sulphoxides containing <11 carbon atoms), after which it drops sharply owing to rapid increase in the solubility of the complex in the aqueous phase[75]. The increase in solubility is due to formation of a trihydrate of the monosolvate $HCl.3H_2O.S$. With 10 M hydrochloric acid in the aqueous phase about 50% of sulphoxides enter from the organic phase[75]. On prolonged contact (5–6 h) with the concentrated acid, extensive reaction takes place with the sulphoxides[70,77], as indicated by disappearance of the sulphinyl band from the infrared spectra of the complexes and also by direct chemical analysis for the sulphoxide content.

Hydrofluoric, Hydriodic, and Hydrobromic Acids

Hardly any work has been done on the mechanism of the extraction of these acids by sulphoxides. Monosolvates are formed[70,78,79], which may be hydrated. Hydrobromic and hydriodic acids react chemically with sulphoxides as the acid concentration of the aqueous phase is increased[70]. The hydrohalic acids can be arranged in the sequence

$$HI > HBr > HCl > H_2F_2$$

of diminishing extractability by sulphoxides. The sequence may be connected with the type of hydration of the acid anion.

Extraction of Sulphuric Acid

The mechanism of the extraction of sulphuric acid by sulphoxides involves hydration and solvation[80]:

$$H^+ + HSO_4^- + h\,H_2O + q\,S = H_2SO_4 \cdot h\,H_2O \cdot q\,S. \tag{9}$$

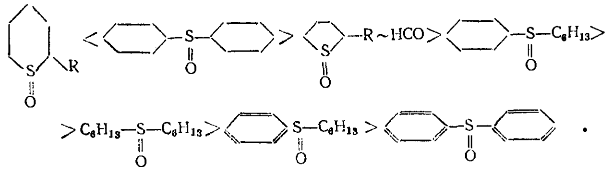
As in the extraction of hydrochloric acid, the solvation and hydration numbers depend on the concentration of acid in aqueous and organic phases. With an aqueous phase containing initially up to 3 M sulphuric acid the latter is present in the organic phase mainly as a dihydrated disolvate $H_2SO_4.2H_2O.2S$; but a trihydrated monosolvate $H_2SO_4.3H_2O.S$ predominates in the organic phase when the acid concentration of the aqueous phase is increased to 5 M, and this complex separates as a third phase; on further increase in the acid concentration it passes into the aqueous phase[80,81]. The displacement of the sulphinyl absorption frequency in the infrared spectra of complexes of sulphuric acid with sulphoxides is about −170 cm^{-1}, which may indicate strong protonation of the sulphinyl oxygen and perhaps transfer of a proton from the acid to this oxygen[45,81] (in concentrated sulphuric acid).

Extraction of Other Acids

Sulphoxides of diverse structure are good extractants for per-rhenic perchloric and boric acids as respectively a disolvate[65], a monosolvate[45,58], and a trisolvate[81]. Sulphoxides—especially those from petroleum—are of practical interest for the extraction of phosphoric acid from sulphuric and nitric acid media, the isolation of boron as boric acid from magnesium chloride solutions, and also the extraction of various heteropolyacids, e.g. molybdophosphoric acid[82].

IV. EXTRACTION OF ORGANIC ACIDS

During recent years several publications have appeared on the use of sulphoxides as extractants for organic acids[83–88]. Monocarboxylic acids are extracted by a solvation mechanism: i.e. unhydrated monosolvates RCOOH.S are formed[81]. The infrared spectra of the solvates show a ν(SO) absorption frequency shift of 20–40 cm^{-1} to longer wavelengths, which indicates formation of a hydrogen bond between the acid proton and the sulphinyl oxygen[89]. As the hydrocarbon group becomes larger, the extraction of the monocarboxylic acid increases, owing to its diminished hydrophilicity and transolvation energy. Extraction of the halogenated acids (such as chloroacetic) is described by Eqn. (6) and also involves formation of unhydrated monosolvates[84,90]. The salting-out effect of cations in the extraction of halogenated carboxylic acids increases with decrease in the ionic radius of the cation and increase in its charge[81]. The heat of extraction of chloroacetic acid by a sulphoxide is ~4 kcal mole^{-1}. The extractive power of sulphoxides for organic acids decreases in the sequence of diminishing basicity of the sulphoxide:



Sulphoxides can be used also to separate organic acids. Thus the partition coefficient of chloroacetic and acetic acids after a single stage of extraction is 20. Most dicarboxylated acids are extracted as anhydrous disolvates—e.g. $(COOH)_2.2S$, $CH_2(COOH)_2.2S$, etc.—produced by hydrogen bonding. Exceptions are phthalic and maleic acids, which form monosolvates on extraction with sulphoxides. The mechanism of the extraction of keto-acids (pyruvic, oxoglutaric) is the same as in the extraction of mono- and di-carboxylic acids. However, the extraction of hydroxy-acids by sulphoxides involves formation of hydrated solvates[86], and the partition coefficient D is smaller than with monocarboxylic acids.

The extraction of organic sulphonic acids by sulphoxides has features in common with that of sulphuric acid: the mechanism of hydration and solvation gives complexes soluble in both aqueous and organic phases, and the sum of hydration and solvation numbers is 4. Sulphuric acid has a strong salting-out effect on the extraction of sulphonic acids. The shift of 80–100 cm^{-1} in the absorption band of the sulphinyl group in the infrared spectra of the complexes of sulphonic acids extracted by sulphoxides indicates stronger protonation of the sulphinyl oxygen by sulphonic acids than by mono- and di-carboxylic acids[81].

Sulphoxides are able to form complexes also with organophosphorus acids. Complex-formation constants $\widetilde{K}$ for di-(2-ethylhexyl) hydrogen phosphate with dihexyl sulphoxide and with 2-pentylthian 1-oxide are larger[91] than with tributyl phosphate (respectively 1.1, 1.8, and 0.65).

Thus the extraction of organic acids by sulphoxides exhibits several regularities. Extraction is greater for monocarboxylic than for dicarboxylic acids, and greater for the latter than for tricarboxylic acids containing the same number of carbon atoms. With increase in molecular mass (i.e. size of the hydrocarbon portion) in each series the introduction of halogens—chlorine, bromine, iodine—leads to an increase in the extraction constants, whereas carboxy-, hydroxy-, and sulpho-groups lower the extraction constant. Thus the extraction equilibrium constants for acids with sulphoxides are determined by the energy of transolvation of the acid on passing from aqueous to organic phases. Extraction entails formation of a hydrogen bond involving the sulphinyl oxygen atom. The extractive power of petroleum sulphoxides exceeds those of tributyl phosphate and phosphonates.

V. EXTRACTION OF METALS

1. Extraction of Metals from Nitrate Media

It is now recognised that sulphoxides are effective extractants for salts of rare metals[92-99]. In all such cases the mechanism remains almost unchanged on passing from tributyl phosphate and its analogues to sulphoxides, when the metal cation is directly coordinated to the sulphinyl oxygen[37].

EXTRACTION OF URANYL NITRATE

As with extraction by tributyl phosphate, sulphoxides extract uranyl nitrate into the organic phase as a disolvate[34,100-105] independently of the type of diluent used:

$$UO_2^{2+} + 2NO_3^- + 2S = UO_2(NO_3)_2 \cdot 2S. \tag{10}$$

In conformity with this equation the extraction constant can be found from the formulae

$$K_U = \frac{y_U \cdot dil}{x_U(2x_H + x_U)^2 (s_0 - 2y_U - y_H)^2 \gamma_\pm^3} = \widetilde{K}_U \cdot \frac{dil}{\gamma_\pm^3} = \overline{K} \cdot dil, \tag{11}$$

where K_U, $\widetilde{K}_U$, and $\overline{K}$ are thermodynamic, concentration, and effective extraction constants, x_U and y_U are the equilibrium concentrations of uranyl nitrate in aqueous and organic phases, x_H and y_H are the equilibrium concentrations of nitric acid (or x_H is the concentration of salting-out agent) in these phases, *dil* is a parameter representing the ratio of the activity coefficients of extracted complex and extractant in the organic phase, $\gamma_\pm$ the mean activity coefficient of uranyl nitrate, and s_0 the initial concentration of the extractant.

With increase in the concentration of nitric acid in the aqueous phase the extraction of uranyl nitrate first increases, passes through a maximum, and then falls[43,44], this decrease being due to competition for the free extractant. At a fixed ionic strength the extraction constant for uranyl nitrate and sulphoxides is almost unaffected by the hydrogen-ion concentration[44,104]. Nor is the extraction constant $\overline{K}$ appreciably affected by the length of the hydrocarbon chain in dialkyl sulphoxides from dipentyl to didecyl. Yet increase in the electronegativity of the groups attached to the sulphur atom lowers the extractive power (Fig. 2), which increases appreciably on passing from dialkyl to cyclic sulphoxides[39,105]. Among cyclic sulphoxides that have yet been studied 2-alkylthian 1-oxides possess the greatest extractive power. The properties of the extracted complexes of cyclic sulphoxides with uranyl nitrate change when the alkyl substituent is moved from the α to the β or γ position relative to the sulphur atom. This is apparent in stronger hydration of the complexes and a considerable diminution in their solubility in organic solvents[76]. When an α-alkyl group in thiolan 1-oxide is replaced by cyclohexylmethyl, the solvation number changes, and uranyl nitrate is extracted as a monosolvate $UO_2(NC_3)_2.S$, apparently owing to steric factors[39]. Complexes of uranyl nitrate with di-isopentyl sulphoxide also show a limited solubility in organic diluents[106], which may be due to polymerisation or to different lattice energies of complexes formed with sulphoxides of differing structure. The variation of the properties of the complexes and especially their solubility require separate investigation.

The extractive power of sulphoxides diminishes considerably with rise in temperature. Heats of extraction calculated from the dependence of $\overline{K}$ on $1/T$ remain almost unchanged on passing from dialkyl to cyclic sulphoxides. As mentioned above, the Reviewers attribute the enhanced extractive power of cyclic sulphoxides to entropy factors[40].

The effect of the solvents for the sulphoxides is well described by the parameter *dil* in Eqn. (11), as in the extraction of uranyl nitrate by neutral organophosphorus compounds. The extractive properties of sulphoxides deteriorate in the sequence heptane–benzene–tetrachloromethane–chloroform. The reason for the impairment in the case of chloroform is its strong solvating action resulting from strong hydrogen bonding with sulphoxides[107].

EXTRACTION OF OTHER METALS

Zirconium and hafnium nitrates are extracted by sulphoxides as disolvates[108], and rare-earth metals (lanthanides) as trisolvates, perhaps partly hydrated in the organic phase[109]. Thorium nitrate is able to form with sulphoxides two solvates—a trisolvate in the presence of a large excess of free extractant[110], and a disolvate in other cases[108].

Gold(III), mercury, silver, and palladium(II) also are extracted by sulphoxides from nitric-acid solutions[36,37]. In contrast to other complexes, however, the last may involve coordination of the sulphinyl group at both sulphur and oxygen atoms, as is indicated by displacement of the sulphinyl absorption band to higher frequencies in the infrared spectrum[48].

Since sulphoxides surpass tributyl phosphate in extractive power, they extract several hydrolysed species of metal salts from nitrate and weakly acid media[111], according to the equation

$$M^+ + (z-m)\,A^- + (h+m)\,H_2O + q\,S \rightleftarrows M(OH)_mA_{z-m}\cdot H_2O\cdot q\,S + m\,H^+. \qquad (12)$$

Hydrolysed species of bismuth(III), iron(III), copper, cobalt, and nickel are well extracted from nitrate media by sulphoxides, and to a less extent those of zirconium and hafnium. The solvation numbers are 3 for copper and bismuth[112] and 4 for iron[111]. In the extracted complexes the metal is coordinated by the sulphinyl oxygen atom (except in the case of bismuth[112]) through a water molecule, as is indicated by the small shift (10–15 cm^{-1}) in the absorption frequency ν(SO).

The action of sulphoxides on many elements has been studied by reverse-phase paper chromatography with the sulphoxides as stationary phase and nitric acid as mobile phase[113–115]. The low R_f values for many elements indicate the possibility of effective extraction of several metals by sulphoxides, as well as their use in the analytical separation of metals in industry. Good separation of the metal pairs zirconium–hafnium, uranium–thorium, zinc–cadmium, iron–copper, etc. can be effected by means of sulphoxides.

2. Extraction of Metals from Chloride Media

By analogy with tributyl phosphate sulphoxides may be able to extract metal chlorides by two mechanisms[116]—as coordinatively solvated compounds (solvates)

$$M^{z+} + z\,A^- + q\,S \rightleftarrows MA_z\cdot q\,S \qquad (13)$$

and as complex anions present in ionic aggregates (as metal-complex acids)

$$M^{z+} + m\,H^+ + (z+m)\,A^- + q\,S \rightleftarrows H_mMA_{z+m}\cdot q\,S. \qquad (14)$$

Extraction by the second mechanism often involves the participation of water, i.e. hydration and solvation.

By the first mechanism (at hydrochloric acid concentrations below 5 M) sulphoxides extract as disolvates the chlorides of palladium[117–121], zinc[63], tellurium[108,122,123], thorium[124,125], uranium[34], zirconoium[126,127], hafnium[126], scandium[128], and perhaps lanthanides; and as monosolvates mercury[129] and silver[130] chlorides. All other metals, as well as most of the above with increase in the concentration of hydrochloric acid, are extracted as metal-complex acids by the second mechanism (14).

During extraction by the first mechanism the metals are coordinated directly to the sulphinyl oxygen (palladium is coordinated through the sulphur atom). In the second mechanism extraction is due to interaction of the proton of the metal-containing acid with the sulphinyl oxygen atom. As the concentration of hydrochloric acid in the aqueous phase is increased, the extraction of metals by sulphoxides passes in most cases through a maximum, independently of the mechanism of extraction. The decrease in partition coefficients with increase in the concentration of hydrochloric acid is due both to its coextraction and to formation of highly charged anions of the metal-containing acids, which are extracted less strongly than are anions having a lower charge or neutral[117] species.

Decrease in the extraction of metals is due to the enhanced solubility of the complexes they form with sulphoxides in concentrated hydrochloric acid. Ruthenium(II) chloride behaves rather unusually in comparison with other salts. With increase in the concentration of hydrochloric acid its extraction by sulphoxides diminishes, passes through a minimum (at 2–3 M HCl), and increases afresh. The descending part can be explained by poor extractability of the anionic complexes.

The composition of the complexes formed during extraction by the first mechanism has been established most reliably—$TeCl_4.2S$,[122] $PdCl_2.2S$,[117–121] $UO_2Cl_2.2S$,[34] $ZrCl_4.2S$,[127] $HfCl_4.2S$,[126] $MoO_2Cl_2.2S$,[131] $WO_2Cl_2.2S$,[131] and $SeCl_3.2S$.[128]

In the analysis of extraction equilibria from aqueous hydrochloric acid the most difficult task is to establish the composition of the complexes formed by mechanism (14). The difficulty is to determine the concentration of the free extractant, since hydrochloric acid may be extracted by sulphoxides as three solvates differing in degree of hydration. It is difficult also to allow for the possible extraction of metal-containing acids differing in the composition of the anionic portion (e.g. $CuCl_3^-$, $CuCl_4^{2-}$, etc.). Direct elementary analysis of the complexes obtained by saturation does not always give an unambiguous answer, since higher solvates may also be present in solution.

Knowing the composition of the complexes extracted, confirmed by infrared, Raman, and proton magnetic resonance spectral data, we can confidently accept that the metal-containing acids—$HGaCl_4\cdot H_2O.3S$, $H_2CuCl_4\cdot 3H_2O.2S$, $HFeCl_4.2H_2O.2S$, $HInCl_4.2H_2O.2S$, and $HInCl_4.H_2O.S$ (on saturation)—are extracted by a hydration–solvation mechanism[63]. Thallium is extracted as the acid $HTlCl_4.2S$ by a solvation mechanism.

From the results of reverse-phase chromatography (with hydrochloric acid as eluant) and the low R_f values for most elements[113,114] it may be concluded that sulphoxides will find application for the extraction of noble metals and certain non-ferrous and rare metals. Large separation factors have been obtained by the use of sulphoxides for the elements selenium–tellurium, molybdenum–tungsten[131], iron–cobalt–nickel[132], tantalum–niobium[133], palladium–rhodium, platinum, etc.

Summarising the results for the extraction of metals from aqueous hydrochloric acid by sulphoxides, we must emphasise that extraction equilibria for this system are still difficult to describe quantitatively—in the sense of interpreting the mechanism of extraction and the formation of extractable complexes—because the aqueous phase may contain several complexes of the same metal, differing in composition and extracted by different mechanisms.

3. Extraction of Metals from Mixed Media and by a Mixture of Extractants

Zirconium, hafnium, uranium[76,134], and thorium are well extracted by sulphoxides from mixed aqueous hydrochloric and nitric acids. As when tributyl phosphate is used, the partition coefficient for zirconium and hafnium is greater from the mixed solutions than from either acid separately[38]. This effect can be explained by enhanced extraction of a mixed complex of the type $ZrCl_n(NO_3)_{4-n}.2S$.[135]

From aqueous sulphuric acid containing a fluoride tantalum and niobium are effectively extracted by sulphoxides[53,136–147] as fluorotantalic and fluoroniobic acids. In most cases these metals form on extraction monohydrated trisolvates of the types $HTaF_6.H_2O.3S$ and $H_2NbOF_5.$ $.H_2O.3S$. Concentration extraction constants of petroleum sulphoxides for tantalum and niobium are respectively 10 and 2.5. These sulphoxides can be used to separate the metals by extraction[53].

Tellurium is extracted as a chloride complex from aqueous sulphuric acid containing a chloride, but the mechanism of extraction has not yet been studied in detail.

Sulphoxides in synergistic mixtures. Comparison of the general laws of the extraction of metals by sulphoxides and by neutral organophosphorus compounds suggests that sulphoxides should have an enhancing effect as donor additions to synergistic mixtures of extractants. Indeed, constants for addition of the first and second molecules of dibutyl sulphoxide to europium tris(2-thenoyltrifluoroacetone) [$Eu(TTA)_3$] [148] are closely similar to or slightly higher than those for tributyl phosphate. In the extraction of uranium by an equimolecular mixture of a sulphoxide and bis-2-ethylhexyl hydrogen phosphate[149] three types of complex—$UO_2A_2.2HA$, $UC_2A_2.2S$, and $UO_2A_2.HA.S$, where A is the anion of the acid HA, and S is the sulphoxide—are present in the organic phase. The main reaction responsible for synergism in the extraction[150,151] can be regarded as

$$UO_2^{2+} + H_2A_2 + 2S \rightleftarrows UO_2A_2 \cdot 2S + 2H^+. \qquad (15)$$

The synergistic effect increases with the basicity of the sulphoxide. Partition coefficients of the metal are considerably higher with sulphoxides than when tributyl phosphate is used as the synergistic additive.

It follows from the above discussion that sulphoxides resemble organophosphorus compounds in the mechanism of complex formation during extraction, but differ in a greater tendency to polymerisation (association) in the organic phase. For example, the extraction constants for uranyl nitrate increase with the metal concentration, which indicates at least dimerisation. This difference is apparently due to the highly polar character of sulphoxide molecules (dipole moment ~4, and for tributyl phosphate ~3) and diminished steric hindrance to association (two groups present instead of the three in neutral organophosphorus compounds). The extracted sulphoxide complexes usually dissolve preferentially in organic solvents of high dielectric constant, are less soluble in aromatic solvents, and exhibit limited solubility in alkanes. It is advisable to use aromatic and chlorinated solvents with sulphoxides as extractants for acids and metal salts.

Study of the chemistry of extraction has shown that sulphoxides—especially those from petroleum—are promising extractants for many radioactive, rare, trace, and non-ferrous metals, as well as inorganic and organic acids. Cyclic sulphoxides (thiolan and thian homologues) possess the strongest complexing power. Since research on the extraction and coordination chemistry of these compounds has only just begun, valuable new data may be expected on the properties of cyclic sulphoxides.

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Complexes of Organosilicon Compounds Containing a Siloxane Bond

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The ability of various classes of organosilicon compounds containing a siloxane (Si-O) bond to form intra- and inter-molecular complexes, by hydrogen bonding and otherwise, is surveyed, and several physicochemical properties of the complexes are discussed. A list of 264 references is included.

CONTENTS

I. INTRODUCTION

Compounds containing a siloxane bond occupy an important place in the chemistry of silicon. Several monographs and reviews[1-3] have dealt with the physical and chemical properties of these compounds, as well as aspects of their practical use. Nevertheless, no survey has yet appeared of the tendency of various classes of such organosilicon compounds to form complexes, with a discussion of their properties. A probable reason is that most studies of complexes of oxygen-containing silicon compounds have appeared during the past decade, although the first compounds of this type were obtained as early as the beginning of the present century[4-6]. Not only are complexes of organosilicon compounds containing a siloxane bond of obvious theoretical interest but attention has recently been paid to them as products of practical promise. Several of them are specific catalysts[7], biologically active compounds[8,9], or intermediates in the production of siloxane oligomers and polymers[10-12].

In contrast to a carbonyl bond, both atoms forming a siloxane bond can act as centres of complex formation. The presence on the silicon atom of five vacant $3d$ orbitals is responsible for the possible existence of five- and six-coordinated silicon compounds. Of the five d orbitals only the d_γ orbitals ($3d_{z^2}$ and $3d_{x^2-y^2}$) are used for the formation of σ bonds, probably for steric reasons. In five-coordinated silicon compounds, which have a trigonal bypyramid structure, p orbitals of other atoms are bonded with the d_{z^2} orbital of the silicon atom (hybridisation of the latter sp^3d). In six-coordinated complexes, with an octahedral structure, the silicon atom has sp^3d^2-hybridised orbitals[13,14].

Besides σ bonding, the d orbitals of the silicon atom (d_e orbitals) can be used to form $p_\pi{-}d_\pi$ bonds with π systems or with atoms having unshared p electrons (halogens, oxygen, nitrogen, etc.) The latter type of bonding is very characteristic of the siloxane bond itself[2], but this does not prevent several compounds containing this bond from forming intra- and inter-molecular complexes by additional $p_\pi - d_\pi$ interaction, as will be shown below.

The oxygen atom acts as another centre of complex formation by the siloxane bond. Owing to $p_\pi - d_\pi$ interaction with the adjacent silicon atom the basicity of a siloxane oxygen atom is usually weak. The degree of $p_\pi - d_\pi$ interaction depends significantly on the structure of the molecule containing the siloxane bond. In the series of compounds CH_3OCH_3, SiH_3OCH_3, SiH_3OSiH_3, for example, the El–O–El′ angle (El, El′ = C, Si) is respectively 111.43°, 120.6°, and 144°, so that the hybridisation of the oxygen atom in methoxysilane can be assessed as intermediate between sp^3 and sp^2, and that in disiloxane as intermediate between sp^2 and sp. In the latter case both lone pairs of electrons of the oxygen atom may take part in $p_\pi - d_\pi$ interaction with d orbitals of the two attached silicon atoms[2]. These compounds, of course, exhibit different tendencies to complex formation both with electron acceptors and with electron donors, as well as with compounds containing active hydrogen or deuterium. One of the main tasks of this Review will be to examine such regularities.

II. COMPLEXES WITHOUT HYDROGEN BONDING

1. Intramolecular Complexes

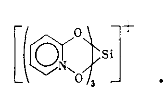
The first intramolecular oxygen-containing organosilicon compounds were obtained in 1903 by Dilthey[4,5], who found that silicon tetrachloride acted on acetylacetone and its methyl derivative to form crystalline substances, which were regarded as "siliconium salts"

$$\{[RCOCH{=}C(CH_3)O]_3Si\}Cl \cdot HCl$$

containing a sexivalent silicon atom (R = CH_3 (I), C_2H_5). These compounds were converted further into salts $[A_3Si]^+M^nCl_{n+1}$, where M = Sn^{2+}, Fe^{3+}, Au^{3+}, Pt^{5+} and A = $RCOCH:C(CH_3)O$.[4-6] Corresponding derivatives of other β-diketones were obtained later[6,15-17]. The octahedral structure of compound (I) has been proved by resolving its racemate into optically active stereoisomers[15,18]. The chelate structure of (I) has been indicated also by its infrared spectrum, from which the carbonyl band in the region of 1700 cm^{-1} is absent, and has been replaced by a wide band at 1555 cm^{-1}.[19] Absorption in the range 1500–1600 cm^{-1}, which is characteristic of all chelate acetylacetonates of metals, is due to stretching vibrations of $C\overset{\cdots}{=}C$ bonds, and in some cases also $C\overset{\cdots}{=}O$ bonds[20-24].

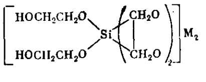
In the proton magnetic resonance spectrum of (I) the signals from protons attached to carbon atoms are displaced down-field relative to the enolic form of pure pentane-2,4-dione, which was initially interpreted as proof of benzoid resonance in the chelate ring[25]. It was shown later, however, that an analogous shift occurs on passing from chelate diketonate cationic complexes of various metals (as well as silicon) to the corresponding neutral diketonates[26,27]. Thus this phenomenon does not indicate the development of aromatic structure in acetylacetonates, and can be satisfactorily explained as an effect of the electric field produced by the charge on the ion[26].

Reports have appeared also of other β-diketonate cationic complexes, having the structure $[\mathrm{SiRdik_2}]^+[\mathrm{M^nCl_{n+1}}]^-$, where $\mathrm{M = H^+}$, $\mathrm{Fe^{3+}}$, $\mathrm{Sn^{4+}}$, and R is a hydrocarbon group[19,24,28], as well as non-ionic compounds $\mathrm{dik_2SiX_2}$, where X is an organic substituent[19], chlorine[19,23,24,29], or an acyloxy-group[21,22,30], and also $\mathrm{dikSiR_3}$, in which R is a hydrocarbon group[21,31-33]. The valency of the silicon atom depends on the composition of the β-diketonates. Chelate rings are present in the cationic complexes $[\mathrm{dik_3Si}]\mathrm{X}$ and $[\mathrm{dik_2SiR}]\mathrm{X}$, as well as in those of types $\mathrm{dik_2SiX_2}$ and $\mathrm{dik_2SiRX}$ (where X represents chlorine on an acyloxy-group)[21-24,28-30,34,35]. Under ordinary conditions stable chelate rings are not formed when two or three organic substituents R are attached to the silicon atom[19,31-33]. Thus expansion of the electron octet with the formation of additional σ bonds occurs only when a sufficient number of electronegative substituents are attached to the silicon atom. In chelate compounds having two diketonate ligands silicon is quinquevalent (trigonal–bipyramidal structure) in the case of ionic compounds, or sexivalent (octahedral structure) when all bonds in the molecule are covalent in character. With dika $\mathrm{SiR_3}$ a chelate structure may merely be intermediate in a *cis–trans* rearrangement[31,32]. A similar structure to cationic β-diketonates is possessed also by siliconium ions having tropolonato-ligands $[(\mathrm{C_7H_5C})_3\mathrm{Si}]^+$ [36,37] and the trispyridine-1,2-dioxysiliconium ion[34]

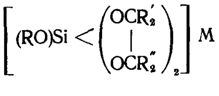


Several other stable ionic complexes are known in which the electron octet of the silicon atom is expanded by the formation of additional SiO bonds. The central silicon atom is attached only to electronegative atoms or in an extreme case may be attached to a single organic group. Typical complexes of this type are derivatives of arylene-o-diols having the structure $[(\mathrm{C_6H_4O_2})_3\mathrm{Si}]\mathrm{M_2.H_2O}$ (where $\mathrm{M = NH_4}$ [38,39], K, $\mathrm{C_5H_5NH}$ [38], $\mathrm{CN_3H_6}$ [40]), $[(\mathrm{C_6H_4O_2})_3\mathrm{Si}]\mathrm{H_2}$ or $[\mathrm{RSi(O_2C_6H_4)_2}]\mathrm{H}$ and their alkali-metal salts[41], $[(\mathrm{C_6H_4O_2})_2\mathrm{Si}]\mathrm{Mg.9H_2O}$ and $[(\mathrm{C_6H_4O_2})_3\mathrm{Si}]\mathrm{Mg}$ [40], $[\mathrm{RSi(O_2C_6.H_4)_2}]\mathrm{NR'_4}$ [34,42,43], and $[\mathrm{RSi(O_2C_6H_{4-n}R'_n)_2}]\mathrm{PR''_4}$.[7] When an organic substituent is attached, the silicon atom is in a five-coordinated state, but in other cases it is six-coordinated. The molar conductance of aqueous solutions of silicon(V) complexes indicates that they are salts formed by a univalent anion and a cation[44].

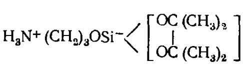
In 1929 Meerwein discovered[45] that orthosilicic esters of glycols and glycerol on titration with caustic alkalis give salts of intramolecular alkoxo-acids, for which a structure of type



was suggested. Later other complexes of similar type

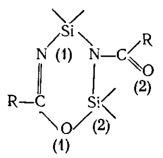

$$\left[(\mathrm{RO})\mathrm{Si}<\begin{pmatrix}\mathrm{OCR'_2}\\ | \\ \mathrm{OCR''_2}\end{pmatrix}_2\right]M$$

were obtained, in which R, R′, R″ = H, Alk and M represents an alkali metal or an ammonium cation[46,47], compounds of corresponding structure with biscyclohexane-1,1-dioxy- and bistetramethylethylenedioxy-substituents attached to the silicon atom[48], and several alkylammonium zwitterions derived from 1,2-diols[49], e.g.


$$\mathrm{H_3N^+(CH_2)_3OSi^-}<\begin{bmatrix}\mathrm{OC(CH_3)_2}\\ | \\ \mathrm{OC(CH_3)_2}\end{bmatrix}_2$$

All complexes of the above type are sparingly soluble in non-polar organic solvents. Several of them are very stable (e.g. the above zwitterion melts at 190°C); others decompose even at 100°C. The formation of complexes is favoured energetically, and often takes place with the evolution of heat. Salts of similar structure have been obtained also from orthosilicic esters of α-hydroxycarboxylic acids[50].

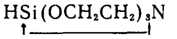
Crystalline adducts of derivatives of monohydric alcohols with five-coordinated silicon, e.g. $[(\mathrm{CH_3O})_5\mathrm{Si}]\mathrm{K}$, $\{[(\mathrm{CH_3O})_4\mathrm{Si}]_2\mathrm{O}\}\mathrm{K_2}$, are stable only at low temperatures[51]. Other examples of intramolecular complex formation by means of additional silicon–oxygen bonds are cyclobisbenzamidodimethylsilane



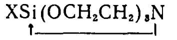
in which the distance between the $\mathrm{Si_{(2)}}$ and $\mathrm{O_{(2)}}$ atoms is 2.613 Å,[52] and also 2,2,5-trimethyl-5-nitro-2-sila-1,3-dioxan, the chair structure of which is assumed to be stabilised by transannular Si ← O interaction[53].

Thus, despite the well defined tendency of the siloxane bond to $p\pi - d\pi$ interaction, leading to diminished electron unsaturation of the silicon atom, the presence of such bonds in the molecule does not prevent involvement of *d* orbitals of the silicon atom in the formation of intramolecular coordinate bonds with oxygen or nitrogen atoms.

A typical example of intramolecular complexes of the latter type is silatrane

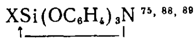

$$\mathrm{HSi(OCH_2CH_2)_3N}$$

with its derivatives

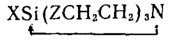

$$\mathrm{XSi(OCH_2CH_2)_3N}$$

where X = Alk, Ar, Hal, etc.[54-80]. These compounds are usually crystalline solids with high-melting points (153 °C for silatrane), although several liquid silatranes have been obtained recently[72,74,75]. The presence of a transannular Si ← N bond in the molecules has been proved by measurements of dipole moments[59-62,81,82], determinations of nuclear magnetic resonance[58,64,65,83,84] and ultraviolet[84] spectra, quantum-chemical calculations[81], and X-ray structural examination[85,86]. According to the latest estimates the transfer of electron density from the nitrogen to the silicon atom in a silatrane molecule is relatively small (0.1–0.2e).[81,82] X-Ray examination indicates that the phenylsilatrane[86] and *m*-nitrophenylsilatrane[85] molecules contain the silicon atom at the centre of a distorted trigonal bipyramid with three equatorial oxygen atoms, whil the axial positions are occupied by the group X and the nitrogen atom. The Si ← N bond lengths in the two derivatives are respectively 2.193 and 2.116 Å, much shorter than the sum of the van der Waals radii of the silicon and nitrogen atoms (~3.5 Å), but exceeding appreciably the length of a normal silicon–nitrogen single bond (~1.83 Å).

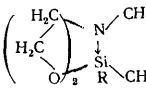
A dative bond Si ← N is formed also in *C*-substituted silatrane derivatives $XSi(OR)_n(OR')_{3-n}N$, where $n = 0-2$, $R = CH_2CH_2$, $R' = CH(CH_3)CH_2$ [60,75,82,87], etc.[75], substituted triphenoxysilatranes

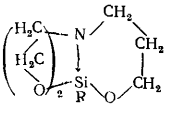

$XSi(OC_6H_4)_3N$ [75, 88, 89]

and other related heterocyclic sytems


$XSi(ZCH_2CH_2)_3N$

(Z = S or NH)[90].


60,64,83,91,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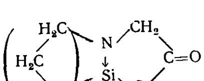
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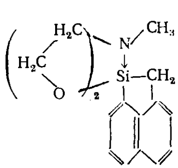
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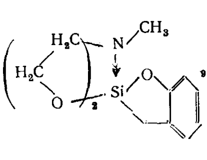
(II)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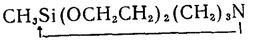
(III)

Available X-ray data indicate that the Si ← N bond length has the values 2.336, 2.344, 2.263, and 2.297 Å respectively for the compound[91]


$CH_3Si(OCH_2CH_2)_2(CH_2)_3N$

for triphenylene-phenylsilatrane[89], and for the above methylbishydroxyethylamine derivatives (II) and (III).[93]

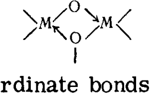
The presence of the Si ← N dative bond is assumed also in phthalocyanine derivatives of siloxanes[94-97].

Transannular Si ← N interaction is almost completely absent from alkyl-2-aminoethoxysilanes $R_nSi(OCH_2CH_2.NR'_2)_{4-n}$.[98-101]

2. Intermolecular Complexes

When dissolved in non-polar solvents the overwhelming majority of compounds containing siloxane bonds (other than silanols) show little tendency to associate or to undergo donor-acceptor interaction with the solvent. This is indicated by numerous determinations of molecular weight and other physicochemical results.

Many heterosiloxanes—compounds containing "foreign" atoms in the siloxane chain—exhibit systematic departures from this rule. Intermolecular coordination of such compounds is due to dative interaction of oxygen atoms with the heteroatoms. The stability of the autocomplexes of heterosiloxanes varies between wide limits. In several cases this type of complex formation is not clearly evident, and is apparent only from some increase in molecular weight. The nature and the valency state of the heteroatom are of decisive importance in the molecular association of heterosiloxanes. Sometimes, however, other substituents attached to the heteroatom and to the silicon atom have an appreciable effect. For example, compounds of the types $[R_3SiOMX_2]_2$ (where R represents H or an organic radical, X = Hal, H, or an organic radical, and M = Al, Ga, In) [102-111] and $[(R_2SiO)_3M]_2$ (R represents an organic radical and M = Al, Ga, Fe) [112-115] form stable dimers having the almost planar four-membered ring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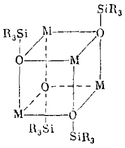
The stability of the coordinate bonds is indicated by that of the ring in $[(CH_3)_3SiOAlCl_2]_2$ (up to 200°C).[108]

An analogous cyclic structure is suggested for $[(CH_3)_3.SiOAu(CH_3)_2]_2$,[116] $[(CH_3)_3SiOTl(CH_3)_2]_2$,[117] and $\{[(CH_3)_3.SiO]_4Zr\}$.[118,119] The presence of three bonds involving the bridging oxygen atoms in the dimers diminishes the strength of $p_\pi - d_\pi$ interaction between silicon and oxygen atoms and confers a coordinatively unsaturated character on the systems. With silanolates of alkali and pseudo-alkali metals, therefore, the above compounds form salts of type $[(R_3SiO)_4M]M'$, whose molecules contain only uncoordinated oxygen atoms, while the heteroatoms M retain their high coordination number[112,114,115,120-125]. The compounds $(CH_3)_3POM[OSi(CH_3)_3]_3$ and $(CH_3)_3NOM[OSi(CH_3)_3]_3$ (M = Al, Ga) probably have the zwitterion structure $\gtrdot\bar{M}-O-\overset{+}{P}\lessdot$.[123] In the crystalline phase potassium, rubidium, and caesium trimethylsilanolates resemble $[(CH_3)_3COM]_4$ in being tetrameric, with the Si–O–M angle 123 ± 2°[126]; trialkylsiloxy-derivatives of mercury, zinc, and cadmium have an analogous structure: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where M = K, Rb, Cs[126] or HgR, ZnR, CdR.[119]

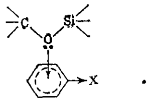
Potassium, rubidium, and caesium trimethylsilanolates are almost insoluble in organic solvents[127-129]. Sodium and lithium silanolates are associated in organic solvents, the degree of association increasing with decrease in the dielectric constant of the medium[128-134]. Potassium trimethylsilanolate dissolves immediately on addition to a solution of lithium or sodium trimethylsilanolate. Pure crystalline double salts $K\{M[OSi(CH_3)_3]_2\}$ (where M = Na, Li), having a narrow melting range, can be isolated from the resulting solutions[127].

Several permethylsiloxy-derivatives of metals have higher molecular weights in solution (degree of association usually $\not>$1.5–1.7). When the methyl groups are replaced by ethyl, however, the degree of association falls to 1.0, probably owing to steric factors[132]. This is typical of compounds of type $U(OSiR_3)_5$ [132], $Zr(OSiR_3)_4$ [118,132], and $Ti(OSiR_3)_4$ [118,133]. Whereas trialkylsiloxy-derivatives of boron, phosphorus, and arsenic are monomeric, the unusual viscosity properties of siloxane polymers containing atoms of these elements suggest that they form unstable donor-acceptor association complexes, which decompose completely on dissolution[134-138].

Besides the above aggregates, complexes of siloxanes with several foreign ligands are also known. The formation of such complexes has been studied systematically by various physicochemical methods (mainly refractometrically)[139-160]. Compounds containing an Si–O–Si group show little tendency to form complexes either with donor or with acceptor solvents. The tendency to complex formation by alkoxysilanes $R_{4-n}Si(OR')_n$ depends on the number and structure of the substituents R and R'. In general the ability of alkoxysilanes to form labile complexes with ligands of any type falls with increase in the number of alkoxy-groups in the molecule and also as their structure becomes more complicated. The weakening of the electron-donating properties of the oxygen atoms observed with increase in *n* in the alkoxysilanes is due to diminished steric accessibility and mainly to diminished polarity of the Si–O(C) bonds caused by the introduction of new electronegative alkoxy-substituents into the molecule. The latter effect is associated with simultaneous increase in $p_\pi - d_\pi$ interaction in the silicon–oxygen bonds. The weakening of the bonds of alkoxysilanes with electron-donating ligands as *n* increases is probably caused mainly by the more difficult steric accessibility of the silicon atom.

Phenoxysilanes, in which substituents more electronegative than alkoxysilanes are attached to silicon, exhibit a greater tendency to complex formation with organic bases, and less tendency with acids [141,146,155]. Oxalyldioxysilanes form stable complexes (up to 80–100°C) with oxolan, dioxan, and pyridine of general formula $[Si(C_2O_4)_2.2X]_n$, and with dioxan also $[C_6H_5Si(C_2O_4H)C_2O_4.1.5diox]_n$. [161]

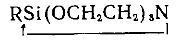
Alkoxysilanes associate with several benzene derivatives of type C_6H_5X. The stability of such complexes increases with the electron-accepting properties of the aromatic ring in the C_6H_5X molecule. Consequently the oxygen atom of the alkoxy-group acts as donor in the charge-transfer complexes formed, and the aromatic compound as acceptor [141,144,146,162]:



Various physicochemical methods have been used to establish the formation of complexes by alkoxysilanes with the tetrachlorides of tin [157,163–168], titanium [169,170], and silicon [171], but not with phosphorus halides [172,173]. Heats of complex formation *q* per donor–acceptor bond in complexes of tin(IV) chloride with $R'Si(OR)_3$ correlate satisfactorily with the sum of the Taft polar σ^* constants of the substituents R′ [166,167]:

$$q = 7.849 - 1.03\,\Sigma\sigma^*;\ r = 0.95\ . \qquad (1)$$

Increase in the +*I* effect of substituents attached to the silicon atom leads to a decrease in the heat of complex formation. The same tendency is evident in the systems formed by titanium(IV) and tin(IV) chlorides with alkoxychlorosilanes $Cl_{4-n}Si(OR)_n$, in which complex formation becomes less marked as *n* decreases [164,166,170]. Silatranes



$RSi(OCH_2CH_2)_3N$

form 1 : 1 and 2 : 1 complexes with titanium(IV) chloride, and an equimolecular complex with aluminium bromide. These complexes are assumed to have an octahedral structure [174].

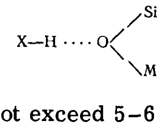
Labile complexes are formed by the interaction of $(CH_3O)_4SiSO_3$, [175] $(C_6H_5O)_4Si$, [176] and $(R_3SiO)_3PO$ (where R = CH_3, C_2H_5, C_6H_5) [177] with dioxan, of alkoxysilanes with iodine [141,156,178], and of alkylalkoxy- and acetoxysilanes with tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium and other paramagnetic shift reagents [179]. Complex formation by aminoalkoxysilanes [180–182] and alkoxyaminosilanes [183,184] with metal halides [181–184] and with silthianes [180] involves the nitrogen atoms, not oxygen.

Donor–acceptor interaction involving a phosphoryl group develops in mixtures of tristrialkylsilyl phosphates with tin(IV) and tellurium(IV) chlorides [185,186] and also with chloroform [177, 186].

III. HYDROGEN BONDING

1. Intermolecular Association of Siloxanes and Alkoxysilanes with Proton Donors

The energy of the hydrogen bond in the associated complexes



(M = Si or C) does not exceed 5–6 kcal $mole^{-1}$. Hydrogen bonds of this type have been studied by infrared spectroscopy [187–220], nuclear magnetic resonance [221], refractometry [140,141,146,152,155,170,199], dielectric measurements [199, 220,222,223], and viscosimetry [140,220]. The proton donors used have been phenol [187–212], pyrrole [188,189,198,212,215], chloroform [141,221,223] or deuterochloroform [214,217], alcohols [140,141, 146,198–200,215,220,222], and other compounds containing mobile hydrogen [141,144,211,216].

Table 1. Shifts in hydroxyl-stretching band of phenol on hydrogen bonding with organo-silanes and -siloxanes.

No.	Formula	$\Delta\nu_{O-H}$, cm^{-1}	Ref.	No.	Formula	$\Delta\nu_{O-H}$, cm^{-1}	Ref.
1	H_3SiOCH_3	183	196	36	$[(CH_3)_3Si]_2O$	169	187
		185	200			170	194
2	$CH_3SiH_2(OCH_3)$	221	196			162	204
3	$(CH_3)_2SiH(OCH_3)$	251	200	37	$(CH_3)_3SiOSi(CH_3)_2n\text{-}C_3H_7$	164	204
4	$(CH_3)_3SiOCH_3$	278	200	38	$(CH_3)_3SiOSi(CH_3)_2\ i\text{-}C_3H_7$	159	204
5	$(CH_3)_3COC_2H_5$	300	187	39	$(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CF_3$	154	192
6	$(CH_3)_3SiOC_2H_5$	271	187	40	$(CH_3)_3SiOSi(CH_2CH_2CF_3)_2CH_3$	147	192
		281	203	41	$(CH_3)_3SiOSi(C_2H_5)_3$	170	192
7	$n\text{-}C_3H_7(CH_3)_2SiOC_2H_5$	286	203	42	$(CH_3)_3SiOSi(C_6H_5)_3$	53	194
8	$i\text{-}C_3H_7(CH_3)_2SiOC_2H_5$	285	203	43	$(CH_3)_3SiOSi(CH_2CH_2CF_3)_3$	*	192
9	$C_6H_5CH_2(CH_3)_2SiOC_2H_5$	270	205	44	$[(CH_3)_2SiH]_2O$	156	187
10	$CF_3CH_2CH_2(CH_3)_2SiOC_2H_5$	255	192	45	$[C_2H_5(CH_3)_2Si]_2O$	190	194
11	$ClCH_2(CH_3)_2SiOC_2H_5$	238	187	46	$[CF_3CH_2CH_2(CH_3)_2Si]_2O$	145	192
12	$CH_3(CF_3CH_2CH_2)_2SiOC_2H_5$	235	192	47	$[ClCH_2(CH_3)_2Si]_2O$	59	187
13	$(CF_3CH_2CH_2)_3SiOC_2H_5$	210	192			65	194
14	$(C_6H_5)_3SiOC_2H_5$	222	187	48	$[Cl_2CH(CH_3)_2Si]_2O$	55	194
15	$(CH_3)_3SiOC_6H_5$	177	209	49	$[BrCH_2(CH_3)_2Si]_2O$	75	194
16	$(CH_3)_3SiOCH_2C{\equiv}CH$	227	209	50	$[ICH_2(CH_3)_2Si]_2O$	85	194
17	$(CH_3)_2C(OC_2H_5)_2$	257	187	51	$[CH_3(CF_3CH_2CH_2)_2Si]_2O$	*	192
18	$(CH_3)_2Si(OC_2H_5)_2$	257	187	52	$[(C_2H_5)_3Si]_2O$	200	194
19	$CH_3(CH_2{=}CH)Si(OC_2H_5)_2$	249	202			*	189
20	$(CF_3CH_2CH_2)_2Si(OC_2H_5)_2$	217	192	53	$(C_2H_5)_3SiOSn(C_2H_5)_3$	375	211
21	$(CH_3)_2Si(OC_6H_5)_2$	154	209	54	$[(n\text{-}C_4H_9)_3Si]_2O$	210	194
22	$CH_3Si(OCH_3)_3$	226	209	55	$(CH_3)_3SiO[Si(CH_3)_2O]_2Si(CH_3)_3$	142	187
23	$CH_3C(OC_2H_5)_3$	201	187	56	$(CH_3)_3SiO[Si(CH_3)_2O]_3Si(CH_3)_3$	137	187
24	$CH_3Si(OC_2H_5)_3$	237	187	57	$[(CH_3)_2SiO]_3$	167	204
25	$C_6H_5CH_2Si(OC_2H_5)_3$	232	212	58	$[(CH_3)_2SiO]_2]CH_3\text{-}n\text{-}C_3H_7SiO]$	167	204
26	$ClCH_2Si(OC_2H_5)_3$	214	212	59	$[(CH_3)_2SiO](CH_3\text{-}n\text{-}C_3H_7SiO)_2$	170	204
27	$C_6H_5Si(OC_2H_5)_3$	224	212	60	$[CH_3\text{-}n\text{-}C_3H_7SiO]_3$	172	204
28	$CH_2{=}CHSi(OC_2H_5)_3$	229	202				
29	$CH_3Si(OC_6H_5)_3$	115	209	61	*cis*-$[CH_3(CF_3CH_2CH_2)SiO]_3$	131	192
30	$C(OC_2H_5)_4$	164	187	62	*trans*-$[CH_3(CF_3CH_2CH_2)SiO]_3$	129	192
31	$Si(OC_2H_5)_4$	219	187	63	$[(CH_3)_2SiO]_4$	144	187
32	$Si(OC_6H_5)_4$	105	209			145	204
33	$(H_3Si)_2O$	*	200	64	$[(CH_3)_2SiO]_2[CH_3\text{-}n\text{-}C_3H_7SiO]_2$	149	204
34	$[(CH_3)_3C]_2O$	329	187	65	$[CH_3\text{-}n\text{-}C_3H_7SiO]_4$	160	204
35	$(CH_3)_3SiOC(CH_3)_3$	261	187	66	$[CH_3(CF_3CH_2CH_2)SiO]_4$	*	192
				67	$[(CH_3)_2SiO]_5$	147	187
				68	$[(CH_3)_2SiO]_6$	141	187

*The basic properties of the oxygen atom do not develop under the conditions of the determination.

Infrared spectroscopy is the most sensitive method for studying a hydrogen bond, whose strength is assessed from the shift $\Delta\nu_{X-H}$ in the X–H or X–D stretching vibrations (X = O, N, etc.) due to interaction of the hydrogen (or deuterium) atom with the siloxane oxygen. According to the absolute frequency shift $\Delta\nu_{X-H}$ proton donors can be arranged in the sequence[189] *p*-bromophenol > phenol > 2,3-dimethylphenol > indole > benzyl alcohol > pyrrole. In interpreting the infrared spectra, however, we must bear in mind that proton donors can form a hydrogen bond not only with the siloxane oxygen atom but also with π-electron systems (aromatic rings, multiple bonds) and halogen atoms present in the proton acceptor[188,224].

Selected values of $\Delta\nu_{O-H}$ for the systems formed by phenol with siloxanes are given in Table 1 together with comparative data for some isostructural organic compounds. Alkoxysilanes are evidently weaker bases than the corresponding dialkyl ethers, and siloxanes are still weaker bases. Thus the oxygen compounds of silicon are much less basic than might be expected from the induction effect of the silicon atom, which is less electronegative than carbon. This is explained by the presence of a donor–acceptor π bond, which diminishes the basicity of the siloxane oxygen atom.

Table 2. Values of $\Delta\nu_{C-D}$, $\Delta\nu_{O-H}$, and $\Delta\nu_{N-H}$, in systems comprising a base and a proton (deuteron) donor, accompanying the hydrogen bonding of compounds of subgroup IV*b* elements with deuterochloroform[214], phenol[216], and pyrrole[215].

General formula	$\Delta\nu_{C-D}$, cm^{-1}				$\Delta\nu_{O-H}$			$\Delta\nu_{N-H}$, cm^{-1}	
	C	Si	Ge	Sn	Si	Ge	Sn	Si	Ge
$(CH_3)_3MOCH_3$	—	—	—	—	153	245	329	163	258
$(CH_3)_3MOC_2H_5$	29	21	38	56	—	—	—	—	—
$(CH_3)_3M]_2O$	33	13	55	84	73	274	—	76	285

Table 2 illustrates the basicity of isostructural oxygen-containing compounds of elements in subgroup IVb. The shifts $\Delta\nu$ are minimal for compounds in which M = Si, owing to the substantial contribution by $p_\pi - d_\pi$ conjugation. Yet the variation in electronegativity of the atom M would suggest that the basicity should increase regularly from carbon to tin. The fall in basicity from compounds in which M = C, Ge, Sn to the isostructural silicon compound is especially large in the $[(CH_3)_3M]_2O$ series.

The departure from this rule observed with n = 3, 4 in the series $R_{4-n}M(OC_2H_5)_n$, where M = C, Si, and R = CH_3 (No. 23, 24, 30, and 31 in Table 1) must be attributed to the great steric hindrance to hydrogen bonding presented by the ethoxy-groups in compounds in which M ≠ C.[198]

Depending on the nature of the compounds the basicity of siloxane oxygen falls in the sequence (Table 1)

$$C_{Alk}OSi > C_{Ar}OSi > SiOSi > SiOSiOSi\ ,$$

which is probably governed by increasing electronegativity of the substituents attached to the oxygen atom and increasing degree of $p_\pi - d_\pi$ interaction in the molecules. A noteworthy feature is the unexpected enhanced basicity of cyclotrisiloxanes (No. 57–62 in Table 1), which is confirmed by nuclear magnetic resonance data[221]. The cause is the lower degree of $p_\pi - d_\pi$ conjugation in the strained planar molecules[188], as well as the greater steric accessibility of the oxygen atoms in them than in higher cyclosiloxanes or linear siloxanes[192].

In series of compounds with the same number of siloxane bonds in the molecule the induction effect of groups attached to the silicon atom has a decisive influence on the basicity. Statistical treatment of experimental data for trialkylethoxysilanes, alkyltrialkoxysilanes, and hexa-alkyldisiloxanes by means of the Taft equation

$$\Delta\nu_i = \Delta\nu_0 + a\Sigma\sigma_i^* \qquad (2)$$

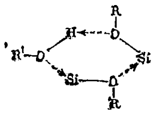
gave the results listed in Table 3. A good linear dependence of $\Delta\nu_i$ on $\Sigma\sigma_i^*$ was shown graphically[207] for phenol complexes of compounds of general formula $(CH_3)_{2-m}(X_nC_6.H_{4-n})_mSi(OC_2H_5)_2$. The variation in the parameter a (Table 3) suggests that the induction effect of the substituents has the greatest influence on the basicity of trialkylethoxysilanes, and the least on that of alkyltrialkoxysilanes, with disiloxanes occupying an intermediate position. Hence the ability of the silicon atom to transmit the induction effect of substituents to oxygen diminishes with increase in the number of siloxane bonds in the molecule. Study of the hydrogen bonding of phenol and pyrrole with compounds of general formula $R_{4-n}M(OC_2H_5)_n$ (where R = CH_3, C_3H_7, n = 1–4, and M = C, Si, Ge) has established that the $\Delta\nu_i$–n lines have smaller slopes for the silicon derivatives than for the carbon and germanium compounds, where p_π–d_π conjugation is either absent or slight[198]. Thus there are grounds for supposing that the diminution in sensitivity to the induction effect of substituents on passing from ethers or alkoxygermanes to alkoxysilanes, or with increase in the number of siloxane bonds in the molecule, is due to increase in $p_\pi - d_\pi$ conjugation in the same sequence[205].

Table 3. Parameters in the Taft equation (2) for complexes of phenol with alkoxysilanes and disiloxanes.

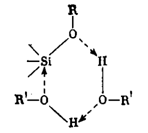
Formula	$\Delta\nu_0$	a	Correlation coefficient	Ref.
$R_3SiOC_2H_5$	275±2	−61.3±3.9	0.980	205
$RSi(OC_2H_5)_3$	237	−24.7	0.992	212
$RSi(OCH_3)_3$	266	−31.8	0.965	212
$(R_3Si)_2O$	162±3	−42.9±3.2	0.954	205

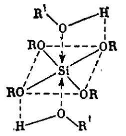
The steric effect of substituents is quite clear in the hydrogen bonding of phenol with siloxanes[189,192,204]. On passing from alkoxysilanes to disiloxanes the influence of steric factors on association with phenol is apparent also in a decrease in the number of hydrogen-bonded hydroxy-groups[192,204]. Differences in tendency to hydrogen bonding depending on steric features of substituents in siloxanes and alkoxysilanes have been revealed also by refractometry[139,141,144] and n.m.r. spectroscopy[221].

Depending on the nature of the components siloxanes and alkoxysilanes may form with proton donors 1 : 2, 1 : 1, and 2 : 1 complexes[145,199,213,220,223]. For example, tetra-alkoxysilanes give only 1 : 2 complexes[220] with the corresponding alcohols, methyltrialkoxysilanes and dimethyldialkoxysilanes 2 : 1 and 1 : 1,[199,213,220], and ethoxytrimethylsilane forms a 2 : 1 complex[195,213]. An ordinary hydrogen bond is undoubtedly present in the 1 : 1 complexes. In other cases silicon atoms may also be involved in complex formation, with an increase in their coordination number to 5 or even 6. For example, a 2 : 1 complex is assigned the structure[199]



and a 1 : 2 complex the structure





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The latter structure is supported by the ability of complexes of tetra-alkoxysilanes with alcohols to dissociate as very weak monobasic acids[199]:

$$Si(OR)_4 \cdot 2\,ROH + ROH \rightleftarrows [Si(OR)_6H]^- + ROH_2^+ \quad .$$

Table 4. Enthalpy of hydrogen bonding of siloxanes and alkoxysilanes with phenol.

Base	$-\Delta H$, kcal mole^{-1}		
	expt.	Ref.	calc. from Eqn.(4)
$[(CH_3)_3C]_2O$	5.9	190	5.9
	7.4	191	
$[(CH_3)_3Si]_2O$	2.9	190	3.3
	4.0	191	
$(CH_3)_3SiO[(CH_3)_2SiO]_3Si(CH_3)_3$	4.3	191	—
$(CH_3)_3SiO[(CH_3)_2SiO]Si(CH_3)_3$	4.3	191	—
$[(CH_3)_2SiO]_3$	4.4	191	3.3
$[(CH_3)_2SiO]_4$	3.2	190	2.9
	3.8	191	
$(CH_3)_3SiOC(CH_3)_3$	6.7	191	4.8
$(CH_3)_3SiOC_2H_5$	6.0	191	5.0

Energetic characteristics published for the hydrogen bond between proton donors and oxygen-containing silicon compounds have been few and contradictory[190,191,195]. Table 4 gives existing values for the enthalpy of formation of the hydrogen bond. A linear relation exists between the frequency shift of the absorption by phenol and the enthalpy of formation of the hydrogen bond, the latter calculated from the association equilibrium constant[190]†:

$$-\Delta H(\pm\,0.5\ \text{kcal mole}^{-1}) = 0.016\ \Delta\nu_{OH} + 0.63 \quad . \qquad (4)$$

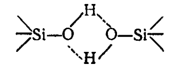
2. Hydrogen Bonds formed by Silanols

Silanols are associated by hydrogen bonding even in very dilute solutions[225-228], so that complete absence of association can be expected only in the gas phase[225,229]. The hydroxyl-stretching frequencies in the infrared spectra of dilute solutions of silanols in relatively inactive solvents (carbon disulphide and tetrachloride) lie in the range 3670–3695 cm^{-1}, being little affected by the nature of the substituents attached to the silicon atom[201,225,229-238]. Absorption by a free hydroxy-group occurs at frequencies 60–80 cm^{-1} higher in silanols than in alcohols[230,239], and is thus closer to the region of vibrations by the hydroxide ion (4200 cm^{-1})[240]. Together with the greater intensity of the band due to a silanol than to a carbinol hydroxyl[238] this indicates that the oxygen–hydrogen bond is more stable in silanols than in their carbon analogues. Hydroxy-groups in gaseous trimethylsilanol[225], as well as those in Aerosil and glass[241-244], absorb at 3735–3749 cm^{-1}. The infrared spectra of concentrated solutions, liquids, or crystals of silanols show a frequency shift to ν_{OH} = 3200 to 3300 cm^{-1},[225,226,229,238,245]. This band due to hydrogen-bonded hydroxysilyl groups has considerable width and greater integral intensity than in the corresponding carbinols.[228] The frequency shift due to association is $\Delta\nu_{OH}$ = 200–400 cm^{-1}, considerably larger than in carbinols, and caused by the enhanced acidity of silanols[187,225,230,231,235,238-240,245]. The absorption frequencies of free and associated OD groups in the infrared spectra of deuterosilanols R_3SiOD are respectively 2710–2730 and 2435–2455 cm^{-1}.[225,229,246]

An interesting example of association due to the hydrogen bonding of silanol groups is heptacyclohexyltricyclo-[7,3,3,1]heptasiloxane-3,7,14-triol, which forms a strongly associated dimer having K_{diss} = 0.0037. This dimer is soluble in benzene and in tetrachloromethane. Its infrared spectrum does not show vibrations of free hydroxy-groups, but contains a broad band with its maximum at 3230 cm^{-1}. It is assumed that all six hydroxyls of the two associated molecules of this triol are hydrogen-bonded in pairs[226].

Still stronger hydrogen bonds are present in the crystals of many inorganic hydrosilicates[241,247-251].

The infrared spectra of crystalline and liquid silanols contain only one wide band due to hydrogen-bonded hydroxysilyl groups[228,235,238,239,245,252], which indicates the cyclic character of the molecular association, in which almost all the hydroxy-groups are involved[228,252]:



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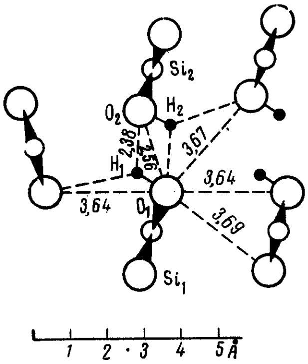

Schematic arrangement of hydroxy-groups in the structure of diethylsilanediol.[255]

X-Ray[253,254] and electron[255] diffraction indicates that crystalline dialkylsilanediols $R_2Si(OH)_2$ (where R represents ethyl or allyl) consist of layers and chains of molecules joined by hydrogen bonds. The accompanying diagram shows schematically the arrangement of hydroxy-groups in diethylsilanediol molecules. The Si-O(H) distance is comparable with the siloxane bond length in polysiloxanes. Some contraction of the $O_{(1)}-O_{(2)}$ bond (2.56 Å) in comparison with the sum of the van der Waals radii can be attributed to the formation by dipoles of a group having a fixed hydrogen bond[225].

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†Values given[191] for ΔH differ substantially from the probably more reliable values in Ref. 190 and from those calculated by means of Eqn. (4).

The infrared spectra of dilute solutions of certain trialkylsilanols containing π-type proton acceptors (phenyl, vinyl) and of all dialkylsilane- and siloxane-diols contain two or more overlapping bands in the region of absorption by hydroxy-groups[232-235,245,252,256]. Their presence can be explained satisfactorily in terms of rotational isomerism[233-235]. The staggered isomers predominate over the gauche isomers (the higher-frequency bands are usually more intense than those at lower frequencies) in $HO[SiR_2O]_nH$ molecules in which $n = 1, 2$ and $R = CH_3$, C_2H_5, whereas with $R = C_6H_5$, $CH_2:CH$ the predominant gauche structure is stabilised by weak interaction of one of the hydroxy-groups with the π electrons of the R substituents. The existence of rotational isomers leads to a certain restriction of freedom of rotation in siloxanediol molecules. The most stable intramolecular bond in hexaphenyltrisiloxane-1,5-diol is due to the steric effect of the phenyl groups, which promote the formation of cyclic, but not linear, molecules. Intermolecular association of polydialkylsiloxanediols is governed by the dimensions of the substituents, and in the case of di- and tri-siloxane-$\alpha\omega$-diols diminishes in the sequence

$$(CH_3)_2 > CH_3(C_6H_5) > CH_3(CH_2:CH) > (C_6H_5)_2.$$

Silanols not only associate but also form complexes with other proton-donating compounds—phenol[187,231,232,257], alcohols[242,243], and water[242,244]—as well as with several electron donors—ethers and esters[200,201,218,219,230-232,257,258], amines[10-12,243,248,258], benzene derivatives[218,219,242,243], dimethyl sulphoxide[201,259,260], ketones[219,243], and others[218,219,242,261,262]—among which study of the complexes with diethyl ether and with phenol gave valuable information on their acid-base properties. Table 5 lists experimental data for the most representative series of silanol complexes. Formation of the complexes with ether and similar compounds undoubtedly involves the hydroxyl hydrogen atom of the silanol, so that their stability is directly dependent on the degree of protonation of the latter. It follows from Table 5 that silanols are significantly stronger acids than analogous hydroxy-derivatives of carbon, germanium, and tin. Similar results have been obtained from a study of complexes formed by these compounds with dimethyl sulphoxide and with oxolan.[200,231] The abnormally high acidity of silanols indicates $p\pi - d\pi$ conjugation between silicon and oxygen atoms with enhancement of the polarity of the oxygen–hydrogen bond[187,196,200,201,230,231,251,263].

The variation of the frequency shift $\Delta\nu_{OH}$ accompanying the hydrogen bonding of silanols with ether indicates that the acidity of the silanols decreases with increase in the $+I$ effect of substituents attached to the silicon atom (e.g. with the lengthening of alkyl groups), but increases with increase in the $-I$ effect. For disubstituted silanediols $R_2Si(OH)_2$ (R = Alk, Ar) the logarithm of the ratio of $\Delta\nu_{OH}$ for the diol–ether to that for the dimethylsilanediol–ether complex is linearly dependent on the Taft σ constants, which confirms the comparatively small contribution by conjugation for most substituted diphenylsilanediols.[257]

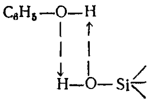
The stability of the ether complexes increases somewhat on passing from trialkylsilanols to the corresponding dialkylsilanediols, which is consistent with replacement of an organic radical by the more electronegative hydroxy-group. Passing from the disubstituted silanediols to the corresponding siloxane-1,3-diols causes little or no (for the methyl or phenyl derivatives respectively) increase in acidity, which remains almost constant on further lengthening of the siloxane chain. These results suggest that the total induction and mesomeric effects of R_2SiO groups ($R = CH_3$, C_6H_5) in the series of compounds $HO[SiR_2O]_nH$ (n = 1–5) are close to zero[232].

Values of $\Delta\nu_{OH}$ for adducts of phenol with hydroxylated compounds (Table 5) indicate that the oxygen atom in the hydroxysilyl group is only slightly less basic than that in a carbinol group, although silanols are significantly stronger acids than are the corresponding alcohols. Triphenylgermanol and triphenylstannol are appreciably stronger bases than is triphenylsilanol, in conformity with the arrangement of the elements in Group IV of the Periodic System. Thus here, too, data for silicon compounds are not consistent with the general rule, probably because of $p\pi - d\pi$ conjugation[201]. In the association of phenol with trialkylsilanols increase in the length of an alkyl group attached to the silicon atom causes an increase in basicity of the hydroxysilyl oxygen atom and hence an increase in the phenolic $\Delta\nu_{OH}$ shift. Replacement of alkyl by more electronegative groups (phenyl, benzyl) leads to diminished basicity. Hence in this series of compounds the more acidic silanols are weaker bases, as might have been expected.

Table 5. Values of $\Delta\nu_{OH}$ in the spectra of silanols (and some of their analogues) in the presence of ether or phenol.

No.	Formula	$(C_2H_5)_2O$		C_6H_5OH	
		$\Delta\nu_{M-OH...O}$, cm^{-1}	Ref.	$\Delta\nu_{C_6H_5OH...O}$, cm^{-1}	Ref.
1	2	3	4	5	6
1	$(CH_3)_3COH$	122	230	271	187
2	$(CH_3)_3SiOH$	238	230	216	230
3	$(C_2H_5)_3SiOH$	230	230	216 228	230
4	$(C_6H_5)_3SiOH$	317	201 231	175	231
5	$(C_6H_5)_3COH$	174	201 231	—	—
6	$(C_6H_5)_3GeOH$	196	201 231	288	231
7	$(C_6H_5)_3SnOH$	10	231	477	231
8	$(C_6H_5)_2HSiOH$	332	230	194	230
9	C_6H_5OH	280	230	132	230
10	$(CH_3)_2Si(OH)_2$	270	232 257	230	232
11	$[HO(CH_3)_2Si]_2O$	275	232 257	268	257
12	$HO[(CH_3)_2SiO]_3H$	274	232	291	232
13	$HO[(CH_3)_2SiO]_4H$	274	232	291	232
14	$HO[(CH_3)_2SiO]_5H$	270	232	230	232
15	$CH_3(C_6H_5)Si(OH)_2$	290	257	—	—
16	$HO[CH_3(C_6H_5)SiO]_2H$	291	257	226	257
17	$(C_6H_5)_2Si(OH)_2$	328	257	—	—
18	$HO[(C_6H_5)_2SiO]_2OH$	328	232	190	257
19	$HO[(C_6H_5)_2SiO]_3OH$	325	232	243	232
20	$CH_3(CH_2{=}CH)Si(OH)_2$	275	257		—
21	$HO[CH_3(CH_2{=}CH)SiO]_2H$	271	257	249	257
22	$HO[CH_3(CH_2{=}CH)SiO]_3H$	275	257	292	257
23	$(C_2H_5)_2Si(OH)_2$	272	257	—	—
24	$(C_3H_7)_2Si(OH)_2$	270	257	—	—
25	$(C_6H_5CH_2)_2Si(OH)_2$	302	257	169	257

On the introduction of new siloxane bonds into silanols the basicity of the latter is not inversely proportional to their acidity, as is always observed with alcohols[257,264]. Thus replacing methyl or phenyl in a trisubstituted silanol by hydroxyl yields the more acidic silanediols, which, however, also possess greater basicity. Acidity remains roughly constant in the series $HO[SiR_2O]_nH$, while basicity increases from n = 2 to n = 3 (Table 5). The shift $\Delta\nu_{OH}(C_6H_5OH)$ suggests that the hydrogen bonding involves hydroxysilyl oxygen atoms, since the shifts produced by the association of phenol with Si–O–Si bonds do not exceed 150–160 cm^{-1}. These results were interpreted in terms of multicentre $p\pi - d\pi$ conjugation, whose development with growth of the siloxane chain may lead to weakening of $p_\pi - d_\pi$ interaction of the hydroxyl oxygen atoms with the terminal silicon atoms[232,257]. However, the unusual apparent relations between the acidity and the basicity of siloxane-$\alpha\omega$-diols may be due to variation in the acidity of phenol itself, resulting from coordination of its oxygen atom with the hydroxy-groups of the siloxane-diol, which are more strongly acidic than phenl itself (Table 5):



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Electrohydrodynamic Atomisation of Liquids

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A critical analysis is given, with a list of 68 references, of the main problems facing the investigation and the application of the electrohydrodynamic atomisation of a liquid.

CONTENTS

I. INTRODUCTION

The production of highly dispersed monodisperse aerosols of similar charge is of great interest both scientifically and for several branches of industry. The vigorous attack on this problem has been due primarily to the use of charged disperse materials in the electronic–ionic industry and to the development of colloidal rocket propellents. Several processes are available for obtaining such aerosols, one of the most promising being the electrohydrodynamic atomisation of liquids, a particular case of electrostatic atomisation. The term "electrohydrodynamic atomisation of a liquid" appeared comparatively recently in certain foreign papers[1-3]. The customary term "electrostatic atomisation of a liquid" covers in essence a number of processes, which can be grouped under three main types of atomisation having characteristic fields of application.

1. Electrostatic atomisation with large mass flows of the liquids (up to ~ 50 cm^3 s^{-1}), with the liquid fed under pressure, and with very high voltages (up to 100 kV and over). The process is accompanied by the formation of a coarsely dispersed polydisperse aerosol. This mode of atomisation has found its greatest application in industrial electrostatic painting.

2. Electrostatic atomisation with minute liquid flows (10^{-9}–10^{-3} cm^3 s^{-1}) and relatively lower voltages (up to 10 kV) in a vacuum. Under such conditions many liquids (from pure dielectrics to molten metals) can be atomised to highly dispersed aerosols of particles having a high ratio of charge to mass ($\geqslant 10^3$ C kg^{-1}). The first account of the production of monodisperse aerosols by vacuum atomisation is that of Semple and Bollini[4]. This process has been applied in rocket technology to produce colloidal propellents and also in microelectronics in the manufacture of printed circuits.

3. Electrostatic atomisation under normal atmospheric conditions with small liquid flows (10^{-8}–10^{-4} cm^3 s^{-1}) and with relatively low voltages on the liquid (3–8 kV). Under certain conditions this process yields a monodisperse aerosol from many liquids over a wide range of droplet sizes (0.1–1000 μm) and with charges on the drops comparable with the limit permitted by the Rayleigh relation for the stability of a charged spherical drop. This is the type of atomisation to which the term "electrohydrodynamic atomisation of a liquid" is mainly applied.

A characteristic feature of the electrohydrodynamic process is that the small mass flows of liquid and the relatively low voltages create identical conditions of formation for all droplets, merely by drops reaching the Rayleigh instability relation $Q^2 = 16\pi r^3\gamma$ (where Q is the surface charge of the drop, r the drop radius, and γ the surface tension of the liquid), which ensures the production of a monodisperse aerosol. This excludes the drawing-out of long continuous liquid filaments (with not too viscous liquids), which in the electric field would disintegrate into separate drops under the influence not only of Coulombic but also of hydrodynamic and gravitational forces, with consequent formation of a polydisperse aerosol. Production of a monodisperse aerosol in the electrohydrodynamic process is superficially analogous to the mechanism of its formation in disc atomisation with extremely small liquid flows.

A considerable number of papers on the investigation and the utilisation of the electrohydrodynamic process have recently been published both here and abroad. The only survey known to the Reviewers is that by Bailey[5]. However, his analysis of published information is insufficiently critical, and he ignores much published work, both recent and earlier, which would give an idea of the state of and prospects for research on the process. We now review and briefly analyse published results on this question.

The first mention of the effect of an electric charge on a liquid dates from 1745, when Bose[6] observed that the rate of cavitation of a liquid in a narrow capillary increases on application of an electric potential. This phenomenon was later explained by the action in a liquid drop of electric forces opposing those of surface tension. When the charge on the drop reaches a certain value, the electric forces become stronger than those of surface tension, and the drop becomes unstable. A criterion of the stability of a spherical drop of an ideally conducting liquid was first established by Rayleigh[7]. The stability of a charged spherical drop in an electric field was investigated by Zeleny[8-10], who evaluated the critical field strength at which the drop still remains spherical. In experimental studies of a corona discharge from a liquid apex[10] he observed that a liquid filament was drawn out from the narrow capillary, and then broke down into separate drops. This can be regarded as the first attempt to investigate the mechanism of the formation of an aerosol by the electrohydrodynamic atomisation of a liquid.

II. MECHANISM OF THE FORMATION OF AN AEROSOL BY THE ELECTROHYDRODYNAMIC ATOMISATION OF A LIQUID

Experimental results indicating the possibility of obtaining a highly dispersed monodisperse aerosol by the electrohydrodynamic method were first published in 1952–1953 by Vonnegut and Neubauer[11,12]. They atomised such liquids as water, sugar solution, lubricating oil, alcohol, suspensions of fine inorganic colorants in poorly conducting liquids, etc., using both direct and alternating voltages of 6–10 kV. The degree of monodispersity and the size of the droplets were assessed from the presence of bright colours in the higher-order Tyndall spectra. Vonnegut and Neubauer determined experimentally for several liquids the upper conductivity limit at which a highly dispersed monodisperse aerosol could still be formed, and stated that a monodisperse aerosol can be obtained even from more highly conducting liquids, but considerably larger drops (of diameter $\geqslant 25\ \mu m$) were then produced. However, these results were not related to the conditions and are of limited value. The authors stated also that a monodisperse aerosol could not be obtained at negative potentials, but offered no explanation. Nor did they attempt to explain the formation of uniform particles, i.e. the mechanism of formation of a monodisperse list, but nevertheless took[11,12] the first step in a theoretical examination of the break up of the initial volume of charged liquid, by adopting an energetic approach to the problem. They put forward the hypothesis of the minimum energy of the system, on the basis that a charged spherical drop (or other finite volume of liquid) tends to a state in which the total energy of the system (the surface energy and the energy of Coulombic interaction of surface charges) is minimal. Such an energy state should correspond to the ensemble of droplets formed when a primary drop breaks up. Examination of the equation for the total energy of the system enables the equilibrium specific charge on the droplets to be determined. For many authors this hypothesis served as starting point in a theoretical investigation of the electrohydrodynamic process[13-15].

The problem of the mechanism by which aerosol particles—in particular a monodisperse aerosol—are formed is undoubtedly basic for an understanding of the physics of the electrohydrodynamic process. It is not surprising, therefore, that many investigators have been concerned with this question. Thus it was suggested[16] that, at the critical potential for the start of fine atomisation (i.e. formation of a monodisperse aerosol), the electric forces of repulsion exceed the forces of surface tension, and the main filament stretching out from the capillary breaks down into a multitude of symmetrically arranged fine filaments, which become unstable and immediately disintegrate into very fine charged drops. Other workers[17,18] have expressed a similar view on the mechanism. The paper on the electrohydrodynamic production of uniform emulsions using an earthed liquid counter-electrode gives photographs of the atomisation process, on which liquid filaments emerging from the capillary can be seen[18]. However, the fairly long exposure in photographing such a rapid process makes unconvincing the authors' statement that aerosol formation occurs by the rupture of filaments extending from the capillary. Furthermore, the comparatively large masses of liquid consumed in the experiments, the conclusion that a highly dispersed monodisperse aerosol can be obtained from non-polar liquids (such as tetrachloromethane), and finally the fact that it was not an aerosol but an emulsion formed by immersing the particles in a liquid that was investigated—in general cast doubt on the reliability of these results.

Some confusion has hitherto existed in many publications concerned in some measure with the mechanism of electrohydrodynamic atomisation and in particular with the formation of a monodisperse aerosol by this process. Thus electrostatic atomisation with large mass flows of liquid has been investigated theoretically and experimentally[19-25]. The high rate of flow, like high viscosity, results in the formation of a stable and relatively long (ten times the drop size) liquid filament, whose subsequent behaviour in the electric field (bending, cleavage into segments, and breakdown of the latter into individual drops) is governed to comparable extents by electrostatic forces and by hydrodynamic and gravitational forces. Yet the results of these investigations have been compared with those obtained for the electrohydrodynamic atomisation of a liquid. Results for atomisation with large mass flows and with very small flows of liquid—the latter involving purely electrohydrodynamic atomisation—should be discussed separately. It is significant that workers who used the latter régime[11,16,17] concluded that a stage in which a liquid filament extends from the tip of the capillary is essential to the formation of a highly dispersed monodisperse aerosol.

In only one paper[26] has the mechanism of the formation of a highly dispersed aerosol by electrohydrodynamic atomisation been regarded as the detachment of single drops from a liquid apex at the tip of the capillary. However, no experimental data were given to support this mechanism. High-speed photomicrographs of the breakaway of a drop and its movement near the capillary showed[27] large drops under a "dropping" atomisation régime with an exposure time lasting milliseconds, so that it is impossible from this paper to assess the formation and the behaviour of the highly dispersed aerosol obtained by electrohydrodynamic atomisation.

The production of monodisperse droplets of size $r = 5-20\ \mu m$ and the formation of an aerosol jet during the electrohydrodynamic atomisation of various liquids (dibutyl phthalate, ethanol, and their 50% solution) have been investigated[28] by high-speed photomicrography using a powerful pulsed laser (20 MW for 35 ns). The experiments showed that formation of a monodisperse mist in this process results from the emission of single droplets from a liquid apex or from the tip of a small liquid cylinder: it is not produced by the stretching out and rupture of a liquid filament, as had been stated earlier[11,16-18,29]. The picture of the process is analogous to the formation of a monodisperse aerosol by disc atomisation with a small supply of liquid.

One of the main problems in the physics of the electrohydrodynamic atomisation of a liquid is to test experimentally the Rayleigh instability relation for a charged spherical drop, as well as to investigate theoretically and experimentally the charges on aerosol particles obtained by this process. A charged electrically conducting spherical drop should retain its size and shape until $Q^2 = 16\pi r^3\gamma$. This relation has been confirmed theoretically[30]. Several workers[31-33] undertook experimental verification by similar methods, consisting in suspending a charged spherical drop in a vertical electric field and observing the moment at which a number of fine droplets were expelled from the surface of the initial drop. This phenomenon was observed in 1926 by Macky[34] in experiments on drops of water placed in a strong electric field. More recently Doyle et al.[31] made a similar experiment on volatile drops. During evaporation the ratio of the surface charge to the mass of the drop increases, and when the Rayleigh relation is reached a cloud of daughter droplets is emitted. These workers found that the charge on the drop at the instant of disruption of its stability agreed quite well with that calculated from the Rayleigh relation.

A second important result from this work was that the charges on the daughter droplets were very roughly measured as half the Rayleigh value, or at least did not exceed the latter. This work[31] was later developed by Abbas and Latham[33]. The application of an original method[35] to measure the size and charge of drops (30–200 μm) of n-octanol obtained by electrohydrodynamic atomisation confirmed also that the drop becomes unstable on attaining the Rayleigh relation and that the ratio of mass and charge lost by the drop also corresponded to this relation. Schweizer and Hanson[32] have shown with almost the same measuring apparatus that the Rayleigh relation is satisfied to at worst 4%, while the losses of mass and charge by the initial drop as a consequence of the emission of daughter droplets are respectively 23% and 5%.

A series of theoretical and experimental studies of the subdivision of a charged drop in an electric field were regarded by Ryce et al.[1,36–39] as applying to electrohydrodynamic atomisation. They were related to the mechanism of the formation of a monodisperse aerosol during atomisation, since they solved the problem of the symmetrical and unsymmetrical splitting of the initial drop as a function of the closeness of its approach to the Rayleigh relation. A theoretical solution was based on the hypothesis of minimum energy[11] with the postulates[36–38] that (i) the resultant droplets do not interact, (ii) the initial drop is able to divide when $Q^2 < 16\pi r^3\gamma$, and (iii) conduction by the surrounding medium is isotropic, i.e. division of the drop is unaffected by the space charge. The solution leads to the conclusion that drops are able to undergo symmetrical cleavage when $Q^2 > 16\pi r^3\gamma$, and unsymmetrical cleavage when $Q^2 \leqslant 16\pi r^3\gamma$. The experimental model involved a large drop of water (d = 2 mm) with addition of a surface-active agent in stearin oil. Since the behaviour of a liquid drop in a gaseous medium differs significantly from its behaviour in a liquid, such a model is quite obviously too remote from the actual process of electrohydrodynamic atomisation. Thus the simplifying postulates in the theoretical solution and the evident incompatibility of the experimental model with the electrohydrodynamic atomisation of a liquid diminish the value of these studies for determining the true mechanism.

Although many investigators have adopted the minimum energy hypothesis for the theoretical assessment of atomisation results, some authors reject it completely. Thus Krohn[2] obtained droplet charges exceeding half the Rayleigh value for the atomisation of Wood's alloy. On the basis of these experimental results and an analysis of the work of Vonnegut, Ryce, Hendricks, and Doyle[31], who employed the hypothesis, he asserts that the minimum energy principle cannot be used to obtain quantitative results and that the droplet charges close to the equilibrium value (i.e. half the Rayleigh charge) found by Hendricks and his coworkers are obviously due to the poor conductance of the liquids employed. He publishes his experimental results, but does not give the method for measuring the parameters of the aerosol obtained, so that it is difficult to judge the reliability of these results.

Until recently the magnitude of the charge on the droplets obtained by electrohydrodynamic atomisation has remained an open question. The most interesting work has been done by Hendricks[40], Pfeifer[3,41], and Semple and Bollini[42]. Experiments by Hendricks et al. on the atomisation of octoil and glycerol showed that the individual charges on drops measured by means of a Faraday cage and a flight-path charge spectrometer agreed quite satisfactorily with the theoretical equilibrium charges and never exceeded them. Semple and Bollini used distilled water as working liquid in their experiments, but accomplished the process under a so called "dropping" régime with monodisperse drops of size 140–420 μm formed with a frequency of 350–950 s^{-1}. As in the above work[40] the charges on these drops were quite close to the equilibrium values, but somewhat exceeded the latter. This result was obviously due to errors of technique, e.g. in the measurement of drop parameters consequent on the difficulty of allowing for evaporation of the drops. The Reviewers have recently shown[43] that the individual charges on monodisperse droplets (5–15 μm) of dibutyl phthalate—a liquid of high boiling point, which eliminates effects due to vaporisation and condensation—are close to the calculated equilibrium value, and at least do not exceed the latter.

Thus, in view of the absence of an exact theory of the electrohydrodynamic atomisation of a liquid, the minimum energy hypothesis can be regarded for the present as a convenient basis for examining (with quite good approximation) qualitative aspects of the phenomenon.

III. POSSIBILITY OF QUANTITATIVE ASSESSMENT OF THE PROCESS

The publication discussed above were devoted to a qualitative examination of the underlying physics of electrohydrodynamic atomisation, but a new line of research—a quantitative appraisal of the possibilities of the method, the relation between the process parameters and the characteristics of the resulting aerosol, and hence the range of possible variation of the process parameters with the aim of controlling the aerosol characteristics—was required for the successful application of the process in colloidal rocket propellents. A physical model for the process must, of course, be chosen before the process can be described quantitatively. We shall therefore consider a few models suggested by different authors.

As mentioned above, the model of a charged spherical drop in an electric field suggested by Ryce is too far from the actual process of electrohydrodynamic atomisation. A model involving periodic variation of the form of a liquid hemispheroid under the influence of an electric field at the tip of a capillary was suggested by de Schon and Carson[44]. Assuming a Poiseuille flow of liquid in the capillary, these authors obtained the dependence of the form factor of the liquid hemispheroid on the time and the parameters of the process—the internal radius and length of the capillary, the height of the hydrostatic column of working liquid, the viscosity of the liquid, and the electric potential applied to the liquid—but neither the electrical conductivity of the liquid nor the size of the droplets obtained was considered. Furthermore, the whole work related to pulsating generation of the aerosol, so that the model cannot be used to describe the production of a monodisperse aerosol, since a pulsating régime does not yield monodispersity[43].

Semple and Bollini[42] describe the production of a collimated beam of monodisperse water drops carrying charges of the same sign. The experimental results gave the dependence of the process on the capillary diameter, the hydrostatic pressure of liquid, and the applied voltage. However, large drops (d = 140–420 μm) were generated, when not only Coulombic forces but also gravity played a significant part ("dropping" régime), so that the model cannot be extended to electrohydrodynamic atomisation.

The most noteworthy papers are those by Hogan and Hendricks[40] and by Pfeifer and Hendricks[41]. In the latter[41] theoretical and experimental investigation of the dependence of the specific charge of the droplets obtained by electrohydrodynamic atomisation on the process parameters the starting point was the minimum energy hypothesis and the authors' model of the mechanism of the emission of droplets of a dielectric liquid from the tip of a capillary in a strong electric field. Both régimes with and those without allowance for the effect of the space charge in the region of atomisation were considered. A formula was obtained[41] for determining the specific charge on the particles from the parameters of the liquid and the process (viscosity, dielectric constant, surface tension, electric potential on the liquid, mass consumption of liquid, geometry of the capillary, and distance from capillary to counter-electrode). Experiments on the atomisation of glycerol yielded an empirical formula for the specific charge on the droplets, which agreed quite well with the theoretical formula. In the deduction of the latter, however, the radius of the liquid tip was equated to that of the capillary in the expression for the strength of the electric field between a liquid point and a plane, which is possible only in the limiting case of an ideal dielectric. In the other limiting case (an ideally conducting liquid) the radius of the tip must obviously be equated to that of the droplet emitted from the liquid tip. This would introduce a correction into the proposed[41] formula.

IV. ROLE OF THE ELECTRIC POTENTIAL AND THE CORONA. NEUTRALISATION OF THE CHARGES ON DROPLETS

Among the main characteristics of electrohydrodynamic atomisation are the initial atomisation potential and the critical potential. The former corresponds to the appearance of instability in the liquid meniscus and the start of atomisation. The critical potential represents the development of the process with increase in the voltage applied to the capillary, and the transition to steady emission of droplets from the liquid point. It has been shown theoretically and experimentally[45,46] that with rise in potential the liquid meniscus is stretched to a cone having a vertical angle of ~ 100°, after which the surface breaks down with the emergence of a liquid filament or with the detachment of droplets from the tip of the cone. The Reviewers have been unable to confirm a theoretical formula obtained[40] for the initial atomisation potential. This formula obviously represents only a particular case of atomisation, and disregards a variety of process parameters and properties of the atomised liquid.

The most interesting characteristic of the generation of a monodisperse aerosol by electrohydrodynamic atomisation is the critical potential[30,43], corresponding to the transition from pulsating generation with formation of a polydisperse aerosol to steady generation of a monodisperse aerosol. The nature of the critical potential can be explained by the variation in the conductivity of the liquid under the influence of the electric field[41], but it is difficult at present to evaluate this potential theoretically.

Since electrohydrodynamic atomisation takes place in strong electric fields, it is accompanied under certain conditions by the development of a corona discharge from the liquid point or liquid filament. Two main problems—the effect of the corona on atomisation as a function of the sign of the applied potential and its effect on the atomisability of the liquid—have been examined in the many studies[2-11,29,35,46-48] of such a discharge from a liquid drop and its effect on electrohydrodynamic atomisation. All experiments on the effect of a corona have been made with potentials of at least 4 kV. A highly dispersed monodisperse aerosol can be generated electrohydrodynamically at the relatively low potentials of 3–4 kV.[28] The process then occurs in the absence of a corona, whether the potential on the liquid is positive or negative.

The liquid droplets formed by electrohydrodynamic atomisation carry a very high charge, approximately half the Rayleigh value, and therefore possess high electric mobility. The rate of electrostatic leakage is then so large that a stable cloud cannot be produced from such an aerosol, while it is difficult to control its transport and formation of an aerosol flux, which entail large losses on the walls of the tubes. In some cases, therefore, the charge and hence the mobility of the droplets must be lowered, sometimes removed completely, or more precisely the aerosol must be brought to an equilibrium charge distribution. An aerosol bearing charges all of the same sign can be neutralised by electrostatic coagulation with oppositely charged particles in the presence or in the absence of an electric field. Such coagulation is more intense only from a certain critical field E_{cr}, which increases with increase in the individual charges on the coagulating particles[49]. Since the individual droplet charges obtained electrohydrodynamically are extremely large, it is pointless in this case to apply an external field to accelerate coagulation.

Several studies of the neutralisation of droplets have used gaseous ions from a corona discharger or a thermal ioniser. Thus the corona discharge with a point–plane electrode system was used[18] to neutralise a cloud of droplets of a polymer solution bearing charges of the same sign. An earthed grid was placed between the corona-displaying point and the capillary to eliminate the effect of the field due to the corona on the field at the end of the capillary. A thermal ioniser—an incandescent tungsten wire—was used[50] to neutralise a flux of charged particles of a water–glycerol mixture, representing the working medium of a colloidal propellent. In this case electrostatic coagulation takes place in the absence of a field.

V. PRODUCTION OF MONOMOBILE AEROSOLS

The need to produce monomobile aerosols—having charges of like sign with a narrow particle distribution function with respect to electrical mobility—arises in many fields of aerosol research as well as in certain special applications of electronic–ionic technology. There is no sharp boundary between mono- and poly-mobile aerosols, as in the case of mono- and poly-disperse aerosols. What aerosol is regarded as monomobile depends on specific requirements. Application possibilities for monomobile and monodisperse aerosols are analogous—calibration of charged-particle counters and spectrometers, investigation of physical processes in charged aerosols, directed deposition of particles in an electric field, etc. Monomobile aerosols located in different mobility ranges are usually obtained by different methods, the chief of which are outlined below.

1. The charging of monodisperse[51] aerosols in the field of a corona discharge (shock charging)[52,53] or in an ionising atmosphere in the absence of an external field (diffusion charging)[54,55]. Many dischargers suitable for the generation of monomobile aerosols have been described[56-62]. Measurement of the particle mobility distribution function

by means of an instrument of high resolving power is the most interesting[62]. Charging by gaseous ions will yield monomobile particles over a fairly wide range of mobilities (0.05–0.0002) with a comparatively high aerosol concentration.

2. The vibrating capillary method with application of a potential to the liquid or induction of charge on the surface of the liquid at the outlet from the capillary. Coarsely dispersed monomobile particles ($d = 120\ \mu m$) were obtained[63], but no quantitative data were given on their mobility.

3. Preparative spectrometry of charged aerosols. Strictly monomobile latex particles were obtained[64], bearing one or more elementary charges.

4. Electrohydrodynamic atomisation to produce a monodisperse aerosol. This provides a very wide range of particle sizes (~ 0.2–700 μm). The individual charges on the particles are very large, around half the Rayleigh limit. The only reported[43] measurement of the mobility of such particles, in which a modified UT 7003 aspiration ion-counter was applied to a monodisperse dibutyl phthalate aerosol of particle size $r = 5–20\ \mu m$, showed that a monodisperse aerosol obtained by electrohydrodynamic atomisation is also extremely monomobile, with the particles of this size range having mobilities of ~ 0.2–0.5 $cm^2\ V^{-1}\ s^{-1}$.

VI. APPLICATION OF THE ELECTROHYDRODYNAMIC ATOMISATION OF LIQUIDS

The possibility of using electrohydrodynamic atomisation to obtain monomobile aerosols having like charges from many liquids—including solutions of organic and inorganic substances, volatile and non-volatile liquids, suspensions, and even melts—guarantees a wide range of applications for the method. Discussion is already proceeding on the possibility of using the process in such fields as colloidal rocket propellents[20,40,41,50], microencapsulation[65], microdosage of very toxic substances[66], preparation of emulsions[17,67], demonstration of electrophysical experiments[68], and, in combination with hydraulic[22-24] and disc[25] atomisation, in electrostatic painting. This method shows great promise for (*a*) obtaining very homogeneous, thin coatings from solutions of polymers, oligomers, and also salts and electrolytes, (*b*) calibrating aspiration counters and ion spectrometers, flow-type charge spectrometers, aerosol classifiers, counters of condensation nuclei, photoelectric aerosol counters, and other aerosol instruments, and (*c*) obtaining and investigating individual polymer molecules by the highly dispersed monodisperse atomisation of extremely weak solutions of the polymers.

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